SYNTHESES and SPECTRAL STUDIES

of

POLYCYCLIC AROMATIC HYDROCARBONS.

THESIS

presented by

Colin Taylor Ironside, B.Sc., (Glasgow)

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ProQuest LLC.
789 East Eisenhower Parkway
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I wish to express my sincere thanks and gratitude to Dr. E. Clar for guidance, help and encouragement during the past three years. This work was possible only with the aid of his long study of and intimate knowledge of this field of chemistry.

My thanks are also due to Professor Akamatu, Dr. Zander, Mr. Carmichael and many other colleagues for their willing co-operation.

Finally, I thank my father for financial support during the first four terms of this work.

C O N T E N T S.

PUBLICATIONS.

The following papers have been, or are about to be, published by E. Clar, C.T. Ironside and M. Zander. Reprints are enclosed at the end.

1. Hexabenzocoronene. Proc. Chem. Soc., 1958, 150.
2. The Electronic Interaction between Benzenoid Rings in Condensed Aromatic Hydrocarbons. 1,12:2,3:4,5:6,7:8,9:10,11-Hexabenzocoronene, 1,2:3,4:5,6:10,11-Tetrabenzoanthanthrene and 4,5:6,7:11,12:13,14-Tetrabenzoperopyrene. J.C.S., 1959 (28) 142.
3. Asymmetric and Symmetric Anellation Effects. Part III, Benzocoronenes.
   Tetrahedron, ~~received January~~ (1959), 4, 358.

Note.

In view of the discussion and conclusions in this thesis, the majority of structural formulae are shown with the greatest possible number of benzenoid sextets, represented by circles. π-electrons not included in these sextets are shown by double bonds.

Introduction.

In the valency-bond treatment of Pauling [1], the Kekule structures of aromatic hydrocarbons have only a statistical significance, while the molecular orbital treatment originally dispensed with them entirely. However, while most chemists have now adopted the view that Kekule structures are wholly unreal, while remaining a useful convenience, recent molecular orbital results reverse this trend and experimental evidence still accumulates to support the classical view.

Clar first predicted [2] that an aromatic hydrocarbon, to be stable, must have at least one Kekule structure. He supported this theory by experimental results [3] and later showed that one Kekule structure is sufficient to produce aromaticity [4]. The calculations of Longuet-Higgins [5] agree with this prediction and those of Dickens and Linnett [6] suggest that the π-electrons in benzene are in fact arranged in three pairs.

Robinson's postulate of the aromatic sextet [7] is intermediate between the extreme delocalisation of the "free electron model" [8] and the localisation implied in classical Kekule structures. It is

supported by Fries' Rule [9] and by the stability and aromatic character of analogous heterocycles, of the cyclopentadienyl anion and of the tropylium cation, which all possess a sextet of π-electrons.

This work studies the spectroscopic evidence on the extent of delocalisation of π-electrons. The initial postulate was that any aromatic hydrocarbon tends to exist in that structure which gives it the greatest number of aromatic or 'benzenoid' sextets.

The synthesis of hexabenzocoronene completed a series of hydrocarbons with 6n π-electrons, n varying from 1 to 7. These can all be written in such a manner that all the π-electrons are located in aromatic or benzenoid sextets, which are connected only by quasi-single or contact bonds. The spectral shifts observed in this series support this structure [10].

The asymmetric anellation effect found in the tetrabenzacene series [11] has now been found also [12] in the benzocoronenes, which can be considered as dibenzoperylene derivatives. This is explained by the theory that each inherent sextet can transfer only two π-electrons to a neighbouring ring which can use them to build up an induced sextet.

These conclusions are supported by measurements of diamagnetic susceptibility [13] which show that the effective radius of the π-electrons is appreciably smaller than the radius of the molecule. Wholly benzenoid hydrocarbons are extremely stable and it appears that there is a greater tendency towards addition reactions when these increase the maximum possible number of benzenoid rings.

Also described in this thesis, is a study of the various dibenzoperopyrenes which can be obtained from the bimolecular condensation of mesobenzanthrone. Attempts to prepare circodiphenyl were not wholly successful, though five new compounds were obtained. The products of bimolecular condensation of naphthanthrone were compared with those from benzanthrone.

A classical synthesis of circumanthracene failed, due to formation of an unreactive stereoisomer of 7',7"-dimethyl-1,9:5,10-diperinaphyleneanthracene. "Controlled graphitisation" gave only small yields of circumanthracene which were not reproducible.

Ultraviolet Absorption Spectra and the Anellation Principle.

Absorption of light by a molecule induces excitation to a higher energy level; the frequency of the light absorbed and the difference in energy of the two states involved are related by the equation :-

$$\nu = \frac{E_2 - E_1}{h.c} \quad .$$

For aromatic hydrocarbons, the differences between electronic levels are of the order of several electron-volts and the corresponding absorption lies in the visible and ultraviolet regions of the spectrum. Vibrational and rotational changes are associated with each electronic transition, so that the absorption spectra show bands and not lines as in atomic spectra. Molecular spectra are thus continuous, though each band can often be resolved into several peaks. The effects of vibration and rotation can be neglected when comparing spectra, by taking the wavelength of the first absorption peak of each band to be characteristic of the electronic transition associated with it. Each band corresponds to a different electronic transition. Hence, classification of the absorption bands of aromatic compounds allows comparison of the energy differences between the same electronic states in different molecules.

Bands can firstly be classified by their position, i.e. by the wavelength of the first peak. More accurate characterisation is given by various properties of the absorption, which are independent of its position: these are- transition probability (which is proportional to intensity of absorption), direction of polarisation [14] (some types of band have maximum intensity when polarised light is absorbed along one particular molecular axis), temperature dependence [15], dependence on solvent [16], and the vibration structure of the bands [16]. Finally, the value of the shift to the red end of the spectrum, in passing from the vapour state to solution and from solution to the crystalline state is characteristic of the individual electronic transitions [17].

The easiest means of classifying bands is the large differences in their intensities. Table 1. gives the classification and characteristics of the first three bands. In this work, Clar's nomenclature of α-, β-, and p-bands is used [18]; these correspond to Platt's ^1L_b, ^1L_a and ^1B_b transitions [19].

Using this classification, Clar discovered the Anellation Principle [18], which states that, in certain series of hydrocarbons, the differences in $\sqrt{\text{Å}}$ between corresponding absorption bands are constant.

Further, the wavelengths of the bands can be calculated by an equation of the type - $\lambda = \frac{K^2}{R}$, where K, the Order Number of the hydrocarbon, is a simple function of the number of π-electrons in it and R is a constant, related to Rydberg's constant. This allows the calculation of the absorption maxima for new or unknown hydrocarbons and is useful for distinguishing between isomers. Known anellation series include, the α-, β-, p-bands of the acenes, p-bands of the perylenes, p-bands of the peropyrenes, etc.

Table 1.

Property.	Band.		
	α-(^1L_b)	p- (^1L_a)	β-(^1B_b)
Extinction coefficient	10^2 - 10^3	10^4- 10^5	10^5
Polarisation: acenes-	long.	trans.	long.
phenes-	trans.	long.	
Temperature dependence.	hypsochromic	bathochromic	
(Shift on going from 20° to -180°C.)	30 -50cm^{-1}	300cm^{-1}	300cm^{-1}
Red shift (Vapour-solution)	250cm^{-1}	900cm^{-1}	900cm^{-1}
Distance between bands.	700cm^{-1}	1300cm^{-1}	1300cm^{-1}.

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Long. = transition moment in direction of the long molecular axis. Trans. = transition moment in direction of the short molecular axis.

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The Importance of the Aromatic Sextet.

One of the most useful tools in ultraviolet spectroscopy is Clar's Anellation Principle [18], which states that in many series of aromatic hydrocarbons, the differences in $\sqrt{\text{Å}}$ between corresponding absorption bands are constant. Series so far found include the α-, β-, p-bands of the acenes, α-, β-, p-bands of the phenes, p-bands of the pyrenes, p-bands of the peropyrenes, etc.

However, the shift of the β-bands is not constant in the series - benzene, diphenyl, triphenylene, dibenzopyrene, tribenzoperylene [20], which can all be written as containing exclusively benzenoid rings, connected by quasi-single or contact bonds. (Since the p-bands vary with the shape of the molecule, they are not suitable for comparison). The properties of these compounds show such resemblance that they must form a true series: they are exceptionally stable, do not dissolve in concentrated sulphuric acid and show strong phosphorescence of very long life at low temperatures. They absorb at shorter wavelength, nearer the violet than any isomeric hydrocarbons, except for the corresponding polyphenyls with the same number of benzenoid rings. It was decided to extend this series by the next two

Table 2.

Hydrocarbon and Ref.	Number of benzenoid rings	Position of first β-band Å	$\sqrt{Å}$	Shift Å	$\sqrt{Å}$.
Benzene (a)	1.	1790V	42.65		
		1819corr.		161	1.85
Diphenyl (a)	2.	1980	44.50	590	6.20
Triphenylene (I) (b)	3.	2570A	50.70	280	2.69
Dibenzopyrene (II) (c)	4.	2850H	53.39	150	1.38
Tribenzoperylene (d) (III)	5.	3000H	54.77	285	2.55
Tetrabenzoanthanthrene (IV) (e)	6.	3340T	57.32		
		3285corr.		252	2.16
Hexabenzocoronene (V) (e)	7.	3600T	59.48		
		3537corr.			

Solvent: V =vapour, A = alcohol, H = heptane,

T = trichlorobenzene.

corr. = corrected for heptane solution;

vapour state --heptane = $-900cm^{-1}$; alcohol --heptane = $0cm^{-1}$; trichlorobenzene --heptane = $+500cm^{-1}$.

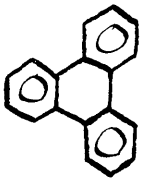
References: (a), Scheibe, Povenz and Lindstrom, Z.phys.Chem., B, 1933, 20, 283. (b), reference 15. (c), Clar, Ber., 1943, 76, 613. (d), reference 20. (e), reference 10.

members, tetrabenzanthanthrene (IV) and hexabenzocoronene (V). The spectral changes in this series [10] are given in Table 2. The changing degree of electronic interaction is shown by the differences in Å, or better, in $\sqrt{Å}$, which is a scale for reciprocal nuclear charges [21].

The shift of the β-band of benzene for the change to diphenyl is 1.85 $\sqrt{Å}$. It is known that the two rings of diphenyl show some conjugation and that the bond joining them has some double bond character. This is shown by the difference in spectrum for non-planar 2,6,2',6'-tetrasubstituted diphenyls [22].

The transition to triphenylene brings a shift to the red of 6.20 $\sqrt{Å}$. This involves the formation of two quasi-single or contact bonds, but, as is shown later, the central ring may possibly obtain aromatic character by transfer of two $\overline{\pi}$-electrons from each of the external rings. A ring may therefore be "benzenoid" either because it contains an inherent sextet of $\overline{\pi}$-electrons, or because it contains an induced sextet, obtained by transfer from the inherent sextets.

This postulate of an induced sextet is here supported by examination of the Kekule structures for triphenylene, of which there are nine, including



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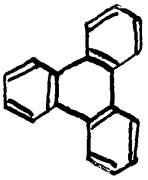
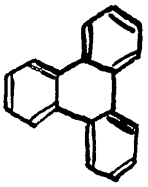


(Ia)



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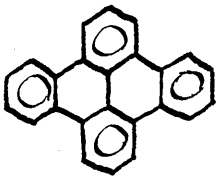

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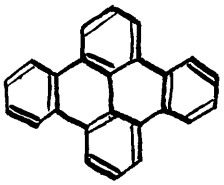
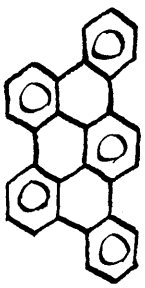


(IIa)



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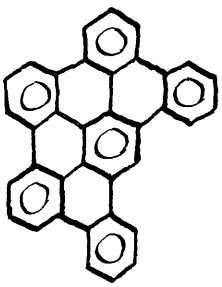

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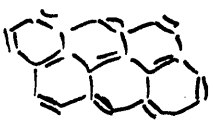
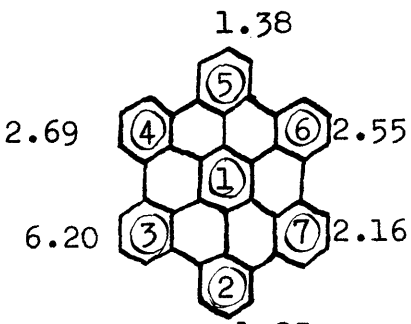


ct n thanthrene



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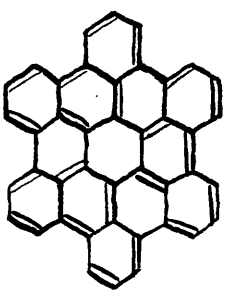


(Va)

(Ia) and (Ib). These show that the central ring can obtain six electrons by sharing and that its bonds can have either single or double bond character, which is a definition of aromaticity. Fries [9] suggested that a structure like (Ia) in which each ring has a sextet of electrons, is the most important. Pauling's method [1] of assuming that all possible structures have equal contributions towards the true state of the molecule is not in full accord. In the next compound, consideration of structures like (IIa) suggests that only one induced ring can be present, which agrees with the spectral shift found. However, any Kekule structure can only give a static picture and an aromatic ring requires a dynamic one. Therefore we denote the aromatic sextet by a circle and try to avoid further mention of Kekule structures.

The shift from triphenylene to 1,2:6,7-dibenzopyrene (II) is 180 Å, corresponding to 2.69 $\sqrt{\text{Å}}$. This is less than twice the shift for formation of the contact bond in diphenyl. Thus the series - diphenyl, triphenylene, dibenzopyrene does not show the constant anellation per ring which is observed in the acene series and others. This agrees with the fact that dibenzopyrene does not behave like a dibenzotetracene. However, this asymmetrical anellation could be

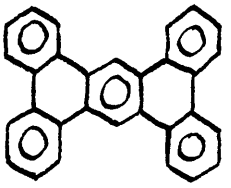
explained to mean that the second anellation produced an induced benzenoid ring and the first formed an empty ring, since a large shift to the red means an increase in reactivity and decrease in stability.

Addition of a fifth benzenoid ring to dibenzopyrene gives tribenzoperylene (III), the shift being 150 Å or 1.38 $\sqrt{Å}$. This is even smaller than the shift for the contact bond in diphenyl.

The next member of the series is tetrabenzanthanthrene (IV) the absorption of which is shifted by 285 Å or 2.55 $\sqrt{Å}$, almost the same as formation of dibenzopyrene (II).

Completion of the series with the hexagonally symmetrical hexabenzocoronene (V) shows a shift of the β-band by only 252 Å or 2.16 $\sqrt{Å}$. This excludes the possibility of a conjugated external frame of alternate single and double bonds, one of the Kekule forms of which is given in formula (Va). Formation of hexabenzocoronene produces three contact bonds and one new ring.

Few other compounds are known which can be represented by wholly benzenoid structures. 1,2:3,4:5,6:7,8-Tetrabenzanthracene (VI) [23] is a member of another wholly benzenoid series which shows the same asymmetric effect as other tetrabenzacenes.



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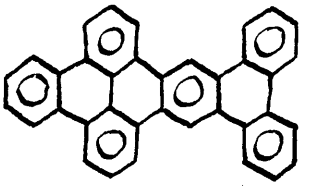

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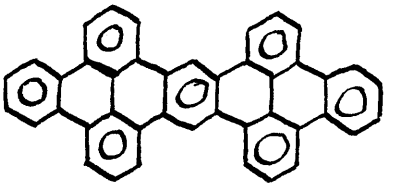

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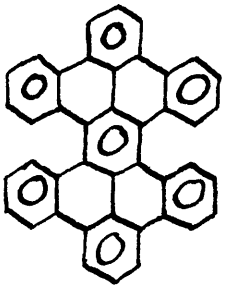

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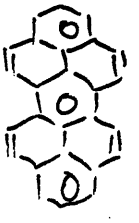


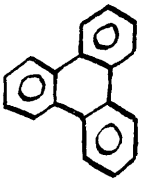
Perylene

This series therefore forms the best approach for extension of this theory to systems which are not fully benzenoid.

Other completely benzenoid compounds which have been synthesized lately are 1,2:3,4:6,7:12,13-tetrabenzopentacene (VII) [24] and 5,6:8,9:14,15:17,18-tetrabenzoheptacene (VIII) [25]. 4,5:6,7:11,12:13,14-tetrabenzoperopyrene (IX) [10] can be written as a fully benzenoid compound, but its spectrum is disturbed by the considerable steric hindrance between overlapping hydrogen atoms.

A suitable field in which to extend the benzenoid theory to hydrocarbons which are not entirely benzenoid, is that of the acenes. The simplicity and regularity of their structure are reflected in the regular anellation shifts found in this series, in which the anellation principle was first discovered [18]. However, series of the type- acenes, 1,2:3,4-dibenzacenes, and tetrabenzacenes, do not show symmetrical shifts for the addition of two angular rings to the starting acene [11].

The first series of this type is wholly benzenoid - benzene, triphenylene, and tetrabenzanthracene (VI). The first shift (8.05 $\sqrt{\text{Å}}$) is more than twice the second (3.40 $\sqrt{\text{Å}}$), although resonance theories expect



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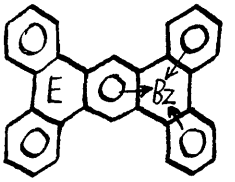
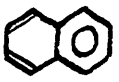
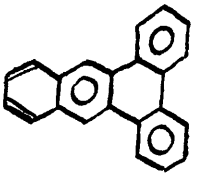


(VI)

λ_β = 1819 —+751— 2570 —+355— 2925 Å.

$\sqrt{\lambda_\beta}$ = 42.65 —+8.05— 50.70 —+3.40— 54.10 $\sqrt{\text{Å}}$.





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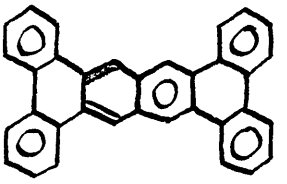
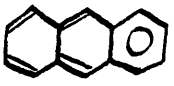
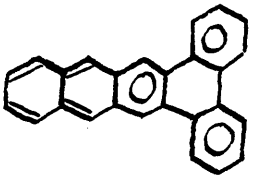


(XI)

λ_β = 2210 —+650— 2860 —+395— 3255 Å.

$\sqrt{\lambda_\beta}$ = 42.01 —+6.47— 53.48 —+3.57— 57.05 $\sqrt{\text{Å}}$.





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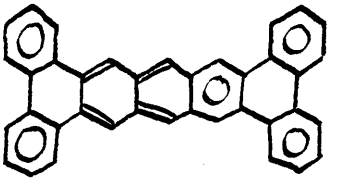


(XIII)

λ_β = 2515 —+615— 3130 —+330— 3460 Å.

$\sqrt{\lambda_\beta}$ = 50.15 —+5.80— 55.95 —+2.87— 58.82 $\sqrt{\text{Å}}$.

them to be equal. An explanation is found when the second shift is deducted from the β-band of triphenylene, which should eliminate the influence of the two angular rings. The result is a β-band at 2237 Å, which nearly coincides with that for naphthalene, which is at 2210 Å in alcohol. Thus one anellation must produce an induced benzenoid ring in "Bz", while the other anellation produces the empty ring "E".

The formation of an induced π-electron sextet in ring "Bz" while leaving ring "E" empty, thus has preference over the symmetrical distribution of π-electrons predicted by the resonance theory. When Robinson first postulated the aromatic sextet, he suggested that each aromatic ring possessed a sextet of π-electrons. Since there is no aromatic sextet in "E", it follows that the central inherent benzenoid ring cannot simultaneously contribute two electrons to both ring "Bz" and to ring "E". This suggests that an inherent ring can share only two π-electrons towards the formation of induced benzenoid rings. This rule is shown below to be general for the acene series and also for analogous perylene series.

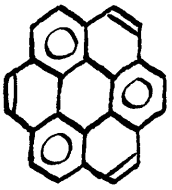
The next series - naphthalene, 1,2:3,4-dibenzanthracene, (X), and 1,2:3,4:7,8:9,10-tetrabenzotetracene (XI), shows exactly the same asymmetric effect. Subtraction of the second shift from the β-band of dibenzanthracene

gives 49.91 $\sqrt{\text{Å}}$ or 2491 Å; the β-band of anthracene is found to be at 2515 in alcohol, and is calculated by the anellation principle to be 2493 Å.

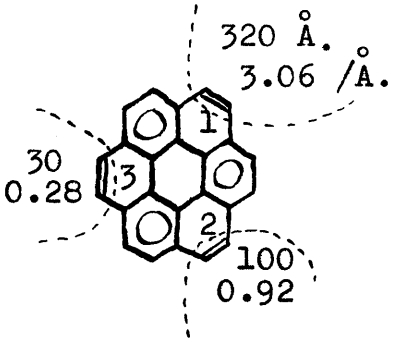
Similarly, in the series - anthracene, 1,2:3,4-dibenzotetracene (XII) and 1,2:3,4:8,9:10,11-tetrabenzopentacene (XIII), deduction of the second shift from (XII) gives 53.08 $\sqrt{\text{Å}}$ or 2818 Å. The β-band of tetracene is at 2740 Å in heptane; the anellation principle predicts it to be at 2802 Å.

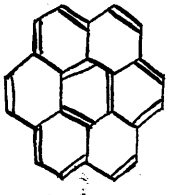
This principle appears to apply to the central acene system of any tetrabenzacene, no matter the length of the acene: this is due to the fact that an acene has only one benzenoid ring with an aromatic sextet, and therefore has only two π-electrons available for sharing towards an induced sextet.

This theory means that each aromatic sextet in a benzenoid ring possesses two π-electrons capable of migration through an acene system, while the other π-electrons are confined to their rings. In contrast, quantum mechanics assumes that all π-electrons move freely in molecular orbitals throughout the whole system [8]. The average π-orbital radius can be estimated from measurements of diamagnetic anisotropy. Akamatu has shown [13] that in polyacenes, the



(XV)



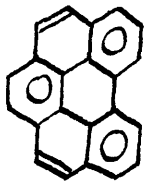


(XIVa)

π-orbital radius tends to a limit: it is 1.71 for pentacene, compared with 1.44 for benzene; the actual radius of the benzene nucleus is 1.39 Å, and the length of pentacene is about 12.14 Å. This confirms a high degree of localisation of the π-electrons of acenes in their rings. In more highly condensed systems [13], the π-orbital radius is larger, though it is always smaller than the value required by completely free movement of π-electrons through the molecule. Table 3 gives some values of the π-orbital radius. The two transferable π-electrons of acenes are probably involved in the addition of protons, and hence determine the degree of basicity of the molecule.

Similar series to those just discussed can be constructed for the step-wise formation of the benzocoronenes, most of which can be derived from perylene. The unknown compounds required for this study have now been synthesised [12].

Coronene itself can be considered to be built up from triphenylene by successive addition of three double bonds, as in formula (XIV). The spectral shifts (of the β-band) due to addition of these double bonds are 320, 100 and 30 Å, corresponding to 3.06, 0.92 and 0.28 $\sqrt{\text{Å}}$. The last addition completes an external frame of conjugated double bonds, as in (XIVa),



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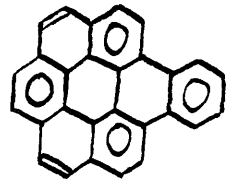
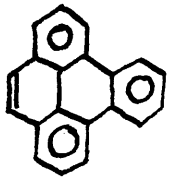


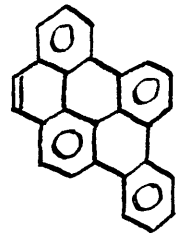
(XVI)

λ_β = 3030 —— +170 —— 3200 Å.

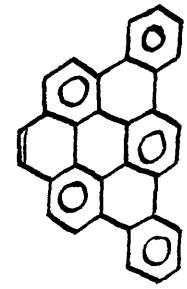
$\sqrt{\lambda_\beta}$ = 55.05 —— +1.52 —— 56.57 $\sqrt{Å}$.



(XVII)



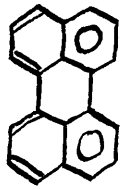
(XVIII)



(XIX)

λ_β = 2920 —— +175 —— 3095 —— +165 —— 3260 Å.

$\sqrt{\lambda_\beta}$ = 54.04 —— +1.60 —— 55.64 —— +1.46 —— 57.10 $\sqrt{Å}$.



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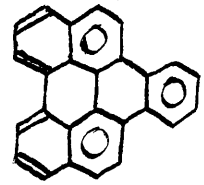
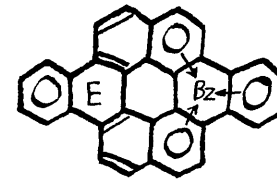


(XXI)



(XXII)

λ_β = 2510 —— +595 —— 3105 —— +173 —— 3278 Å.

$\sqrt{\lambda_\beta}$ = 50.10 —— +5.63 —— 55.73 —— +1.55 —— 57.28 $\sqrt{Å}$.

which should allow rotation of electrons round the perimeter of the molecule and would then cause the largest shift. Since this is not so, the π-electrons must be arranged in a more localised manner, as in (XIV). This conclusion is supported by measurement of the diamagnetic anisotropy [13], which gives the effective π-orbital radius as 1.94 Å. Hydrogenation of coronene produces 1,2:5,6:9,10-hexahydrocoronene [26], which retains the triphenylene nucleus.

The benzo- and dibenzo-coronenes can be built up by the addition of the o-phenylene group to suitable molecules. If these already contain the triphenylene nucleus, a relatively small spectral shift aoccurs, but formation of this nucleus brings a large shift of the β-band to the red.

1,12-Benzoperylene (XV) plus an o-phenylene complex gives 1,2-benzocoronene (XVI); the shift of the β- absorption band is 170 Å (1.52 $\sqrt{Å}$), well below the usual value for formation of two contact bonds.

A similar result is found when two o-phenylene groups are attached to 1,2-benzopyrene (XVII), forming (XVIII) and (XIX). The corresponding shifts are 1.60 and 1.46 $\sqrt{Å}$.

1,2:7,8-Dibenzocoronene (XXII) is built up in an analogous way from perylene (XX) which does not

contain a triphenylene complex. Such a complex is formed in the first addition stage, which produces 1,12-o-phenyleneperylene (XXI). The shift is 595 Å or 5.63 $\sqrt{Å}$, almost the same as that for producing triphenylene from diphenyl (6.20 $\sqrt{Å}$). The second addition produces a shift of 1,55 $\sqrt{Å}$. From its diamagnetic susceptibility, perylene appears to be formed of two naphthalenes [13]; each of these, like any acene, has one pair of transferable π-electrons. These cannot be shared with rings "Bz" and "E" simultaneously.

Here, as in the tetrabenzacenes, deduction of the second shift from the β-band of (XXI) should remove the inherent sextet while leaving the effect of the induced sextet. This gives a value of 54.18 $\sqrt{Å}$ or 2936 Å. The β-band of 1,12-benzoperylene (XV) is at 3030 Å in benzene solution, so that the agreement is not so close in this case, though the difference from perylene (2510 Å) shows that an induced benzenoid sextet has been formed in one of the anellations.

It must be noted that the series - (XVII), (XVIII) and (XIX) shows a symmetric anellation effect; only when a triphenylene nucleus is formed is there an asymmetric anellation effect.

Table 3.

Diamagnetic Susceptibilities[13),27)].

Compound	Mole Suscept. $(-X_M.10^6)$	$/\bar{r}^2$ (Å).
Hydrogen (atomic)	2.93	
Benzene C_6H_6	55.6	1.44
Naphthalene $C_{10}H_8$	92.2	1.57
Diphenyl $C_{12}H_{10}$	103.25 [28)]	
Phenanthrene $C_{14}H_{10}$	127.9	1.61
Triphenylene $C_{18}H_{12}$	156.6	1.55
Perylene $C_{20}H_{12}$	166.8	1.51
Coronene $C_{24}H_{12}$	243.3	1.94
Hexabenzocoronene $C_{42}H_{18}$	346.0	

Calculations.

Contact bond:- $\lambda = X_M(\text{Diphenyl}) - 2X_M(\text{Benzene}) + 2X_M(H)$

$= -2.09$

Hexabenzocoronene:- $(-X_M.10^6)$.

$7X_M(\text{Benzene}) - 24X_M(H) = 318.9$

$7X_M(\text{Benzene}) - 24X_M(H) + 12\lambda = 343.98$

$X_M(\text{Triphenylene}) + 4X_M(\text{Benzene}) - 18X_M(H) = 326.3$

$3X_M(\text{Phenanthrene}) - 12X_M(H) = 348.5$

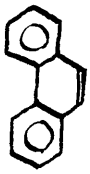
Triphenylene:-

$3X_M(\text{Benzene}) - 6X_M(H) = 149.22$

$3X_M(\text{Benzene}) - 6X_M(H) + 3\lambda = 155.49.$

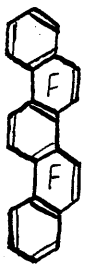
A list of values of diamagnetic susceptibility is given in Table 3. Where the anisotropy has been measured, a value can be given for the average radius of the π-orbital [29]. Pascal has shown [30] that susceptibility is approximately additive: hence, Akamatu [27] suggested that hexabenzocoronene is formed of three phenanthrene nuclei, rather than one triphenylene and four benzenoid rings. However, it is possible to calculate results for triphenylene and hexabenzocoronene which are in good agreement with experimental values by using the value for the contact bond in diphenyl [28] but with the opposite sign.

It is interesting that the contact bond in diphenyl causes a negative increment, and in triphenylene and hexabenzocoronene, a positive one (making no allowance for any induced sextet). A single bond has no effect, double and triple bonds have positive effects and formation of an aromatic ring has a negative effect. Possibly the difference in sign for the effect of the contact bond is connected with the asymmetric spectral shift discussed above, though in this case the odd molecule is diphenyl and not triphenylene.



λ_β = 1819 +691 2510 +386 2896 Å.

$\sqrt{\lambda_\beta}$ = 42.65 +7.45 50.10 +3.71 53.81 $\sqrt{Å}$.



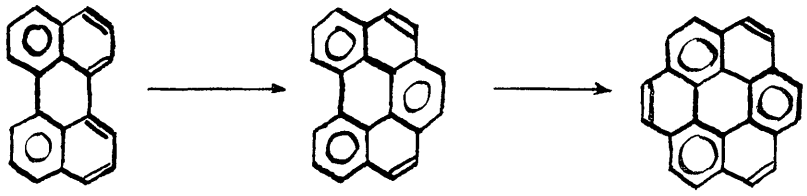
(XXIII)

(XXIV)

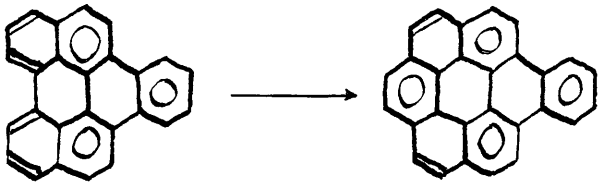
Measurement of the susceptibilities of the other wholly benzenoid hydrocarbons would therefore be very interesting.

Fries' Rule [9] is rather similar to this theory of benzenoidity. It differs in requiring a fixed Kekule structure and in allowing complete sharing of the π-electrons. Thus in picene (XXIII), Fries' Rule suggests that there are two induced benzenoid rings "F". The spectral shifts in the series - benzene, phenanthrene, picene, show strong asymmetry, so that only one induced ring is formed, in agreement with the rule that a benzenoid ring can transfer only two of its π-electrons.

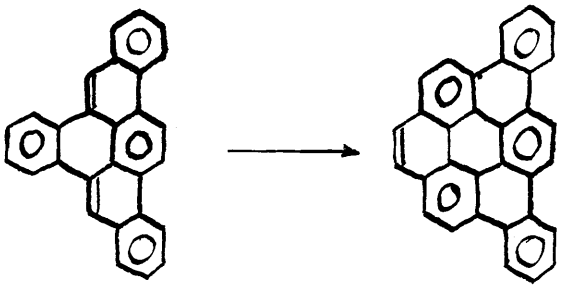
Robinson's original theory of sextets [7] proved very useful for those aromatic compounds which are not hydrocarbons entirely composed of six-membered rings, though it was not at first in an acceptable form [e.g. formula (XXIV)]. The present method of writing sextets as circles actually includes the majority of Kekule structures, but differs from Pauling [1] in giving no importance to the other structures, which produce more conjugation amongst the rings but have less than the maximum possible number of benzenoid rings.



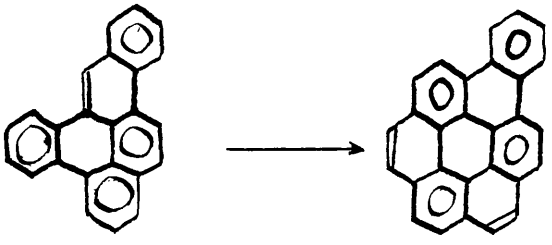
(XX) (XV) (XIV)



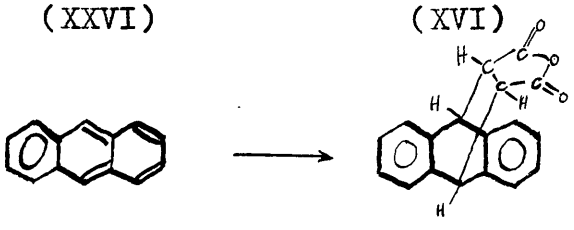
(XXI) (XVI)



(XXV) (XIX)



(XXVI) (XVI)



(XXVII)

Though this theory is in disagreement with quantum mechanical conclusions, this may be due to the statistical nature of the latter method: X-ray determinations of structure also give a statistical picture. On the other hand, spectral comparison selects those molecules which select at the maxima of the absorption peaks; these do not correspond to the "average" molecule but rather to the extreme state. Thus, disagreement with statistical methods does not invalidate these results.

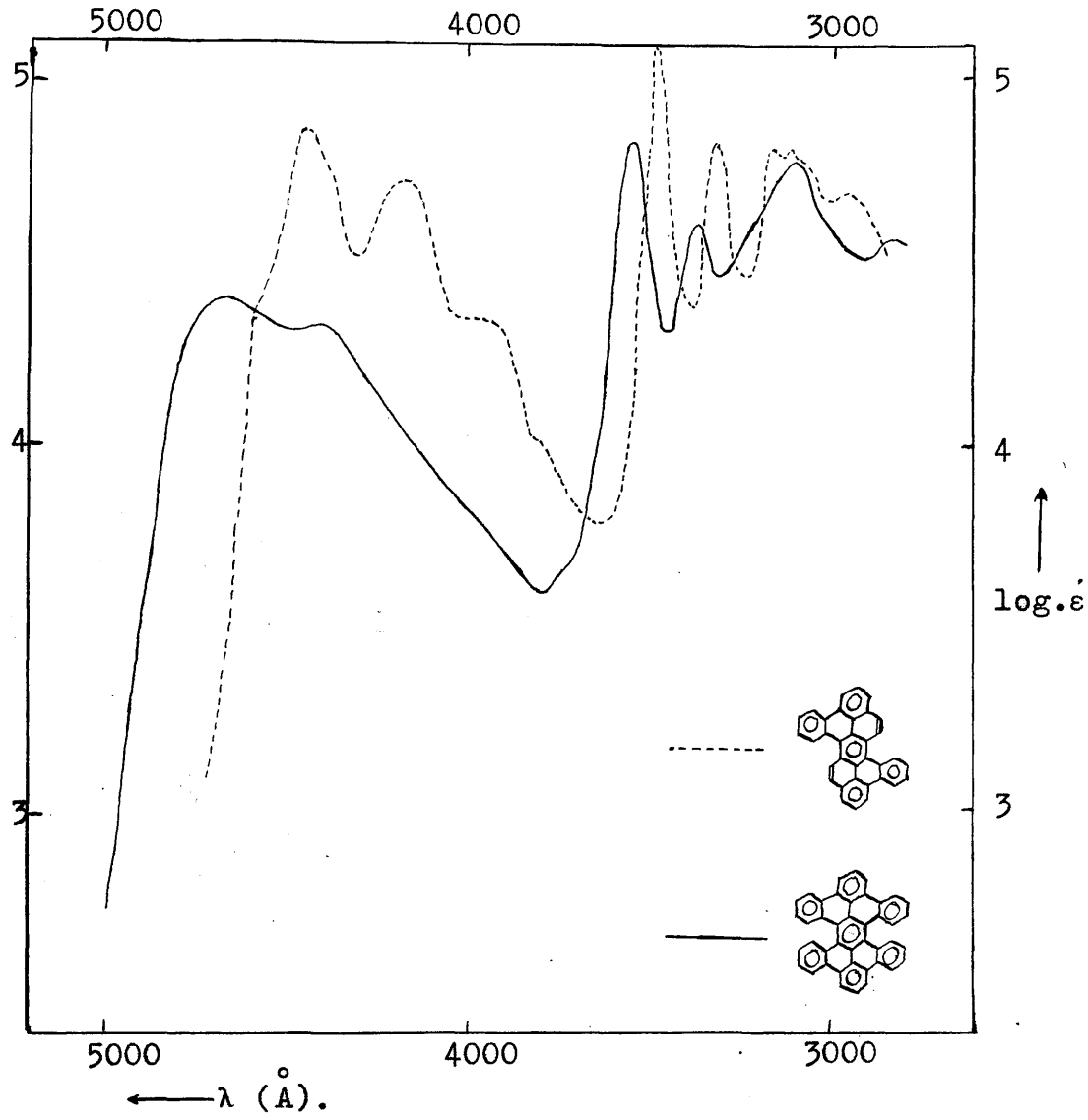
Further support for this theory is obtained from the reactivity of aromatic molecules. These molecules which are fully benzenoid are very stable and unreactive, like benzene itself [10]. Molecules which are not wholly benzenoid usually react as if they contained the maximum possible number of benzenoid sextets, or else react in such a way as to increase this maximum [12].

This is shown most clearly by the addition reactions of maleic anhydride. This addition is much easier for perylene than for 1,12-benzoperylene [31]. in contrast, 1,12-o-phenyleneperylene (XXI) adds maleic anhydride readily to lead to 1,2-benzocoronene, which has one more inherent sextet.[12]. 1,2:4,5:8,9-tribenzopyrene (XXV) reacts twice with maleic anhydride and chloranil as dehydrogenating agent [12], as also does

1,2:4,5-dibenzopyrene (XXVI) [12]. Even after a short reaction, these compounds show no trace of the mono-adduct. Since it is unusual to find a double condensation of this type, it may be explained by the fact that in these cases, double but not single condensation increases the maximum possible number of benzenoid rings with inherent sextets by one. Even when maleic anhydride adds endo-cyclically, as in the higher acenes, it tends to increase the number of inherent sextets. Thus, naphthalene reacts only to the extent of 1% [32], and in the higher acenes reaction takes place in a central ring, so that the system is divided into two acenes, and contains two sextets as in (XXVII) [33].

Synthesis of 1,12:2,3:4,5:6,7:8,9:10,11-Hexabenzocoronene (V) [10),34)].

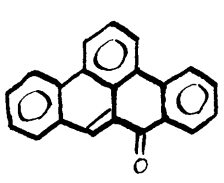
Reductive self-condensation of 1,9:2,3-dibenzanthrone (XXVIII) by means of a melt of zinc dust and zinc chloride [35)], should give hexabenzocoronene plus a mixture of other products. Separation should be relatively easy, because of the differing degree of condensation. However, dibenzanthrone is best prepared from dibenzanthrene (XXIX), so before oxidising this, it was decided to try condensation of the hydrocarbon. Compounds of this type, containing the peri-naphthindene nucleus, form non-paramagnetic complexes with bromine [10),36)]. Dibenzanthrene added three atoms of bromine per molecule; on melting, or on being refluxed in trichlorobenzene, this complex lost three molecules of hydrogen bromide. Only one product was formed; this melted at 482°C with loss of four atoms of hydrogen, resolidified and did not melt again below 700°C. The spectrum of the first compound (Fig. 1) closely resembled that of 4,5:11,12-dibenzoperopyrene and it was concluded to be 4,5:6,7:11,12:13,14-tetrabenzoperopyrene (IX), the only possible product that can lose four atoms of hydrogen by further condensation. It thus produces hexabenzocoronene (V).



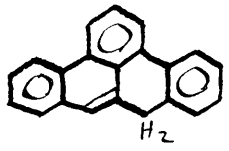
—— 4,5:6,7:11,12:13,14-Tetrabenzoperopyrene (IX), in benzene. Absorption maxima (Å)and log.ε (in parentheses):- 4670 (4.41), 4450 (4.34), 3540 (4.83), 3370 (4.61), 3090 (4.78), 2840 (4.57).

---- 4,5:11,12-Dibenzoperopyrene (LV), in benzene. Absorption maxima:- 4450, 4180, 3980, 3480, 3320, 3165, 3110, 2960 Å.

Fig. 1.



(XXVIII)



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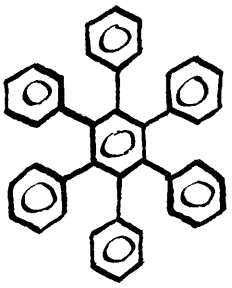

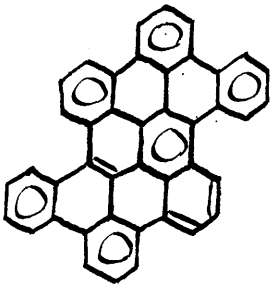

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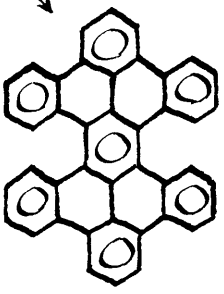

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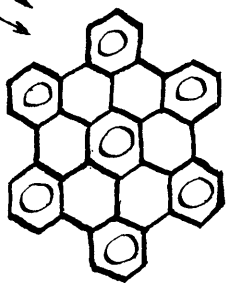

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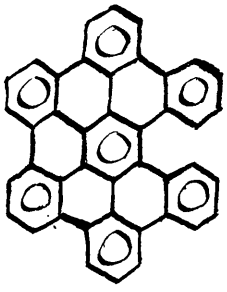

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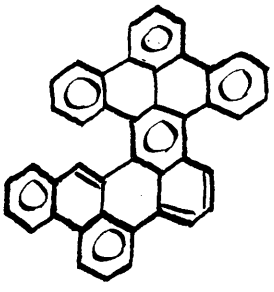

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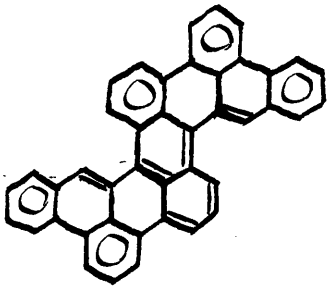
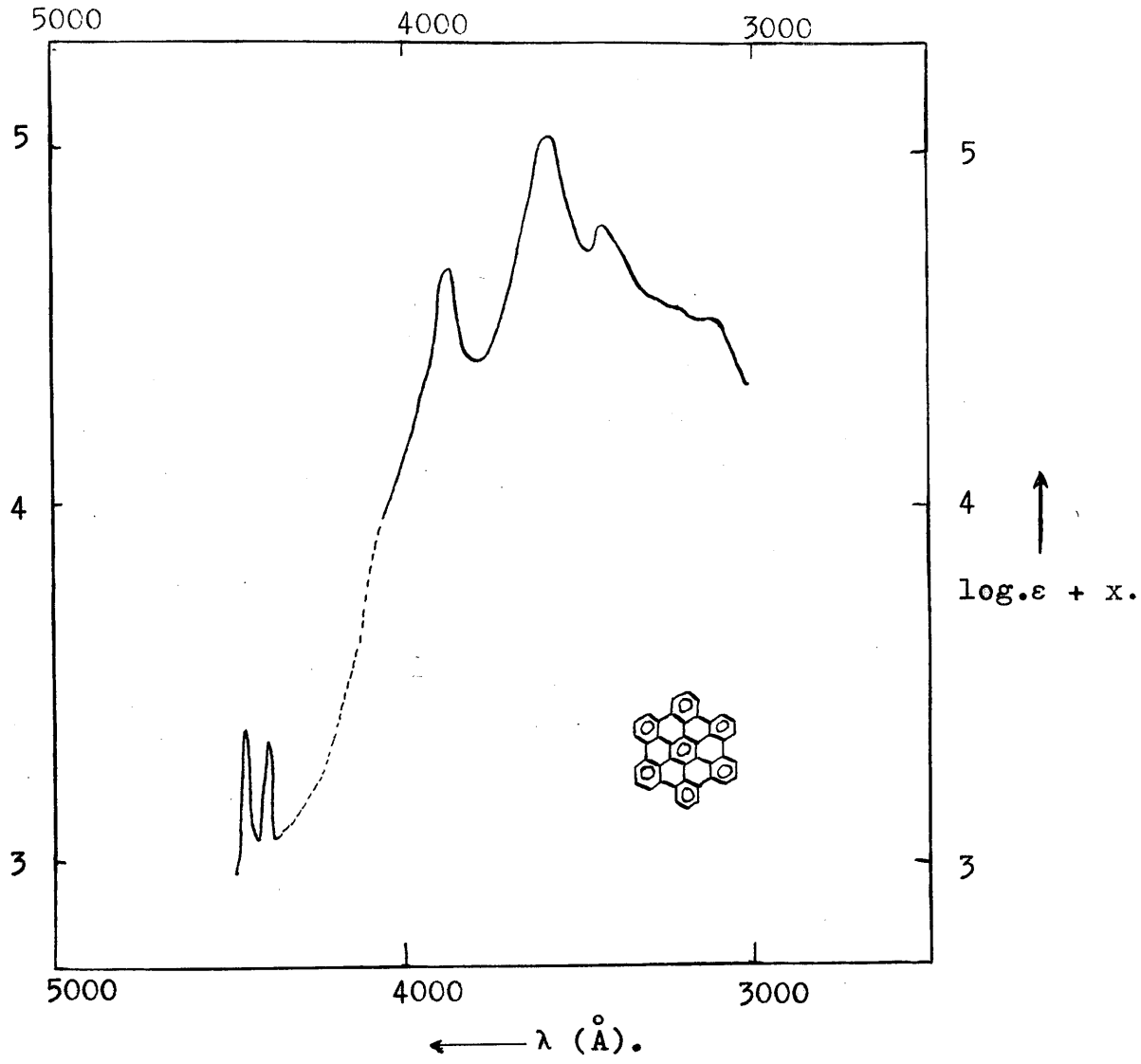


(XXXIII)

Both of these hydrocarbons are extremely stable; they do not dissolve in cold concentrated sulphuric acid and absorb light only in the violet end of the visible spectrum. They show orange-yellow phosphorescence of very long life, in solid solution in trichlorobenzene at -180°C. Hexabenzocoronene was also obtained by melting dibenzanthrene with sulphur, and by sublimation of the residues from the preparation of dibenzanthrene by the Elbs reaction [37]. Its spectrum is given in Fig. 2. The spectrum of tetrabenzoperopyrene shows broadening of the p-bands, due to the twisting caused by the four overlapping hydrogen atoms. Calculation shows that this molecule should prefer a propeller-like shape [38].

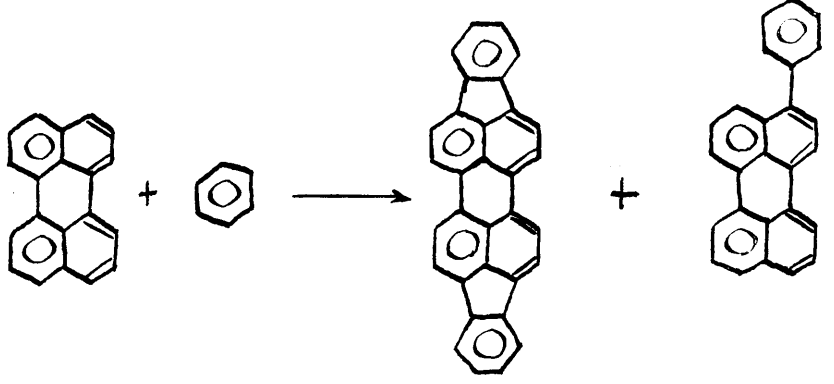
An independent synthesis of hexabenzocoronene has now been published [39]. It was obtained both by the action of aluminium chloride on hexaphenylbenzene and by a zinc dust melt on dibenzanthrone (XXVIII). The latter method also gave tetrabenzoperopyrene (IX) and 1,2:3,4:8,9:10,11-tetrabenzobisanthene (XXX), but none of the other theoretically possible products, (XXXI), (XXXII) and (XXXIII).

The hexabenzocoronene described in this paper agreed in its properties with our own product.



1,12:2,3:4,5:6,7:8,9:10,11-Hexabenzocoronene (V), in trichlorobenzene. Absorption maxima :-
4440, 4380, 3875, 3600, 3425 Å.

Fig. 2.



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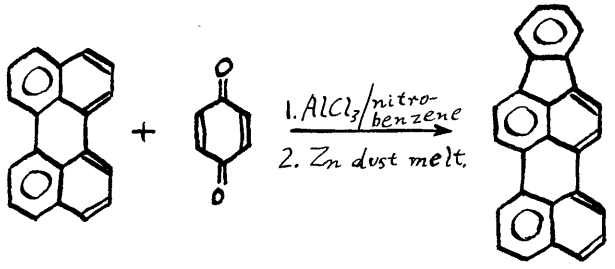
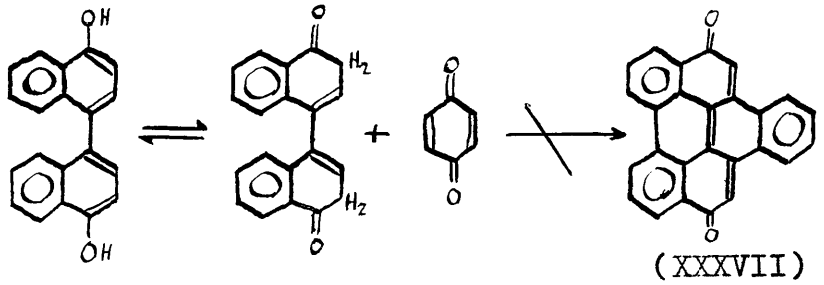
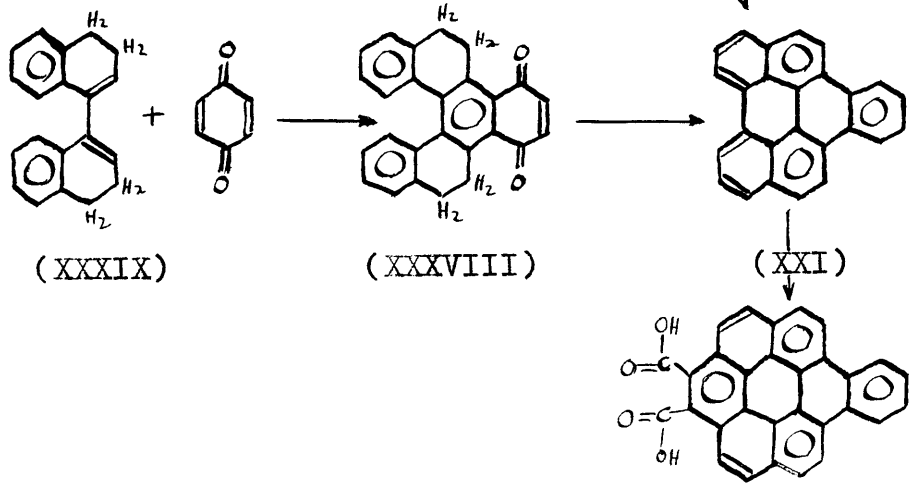


(XXXVI)



(XXXVII)



(XXXIX) (XXXVIII) (XXI)

(XL).

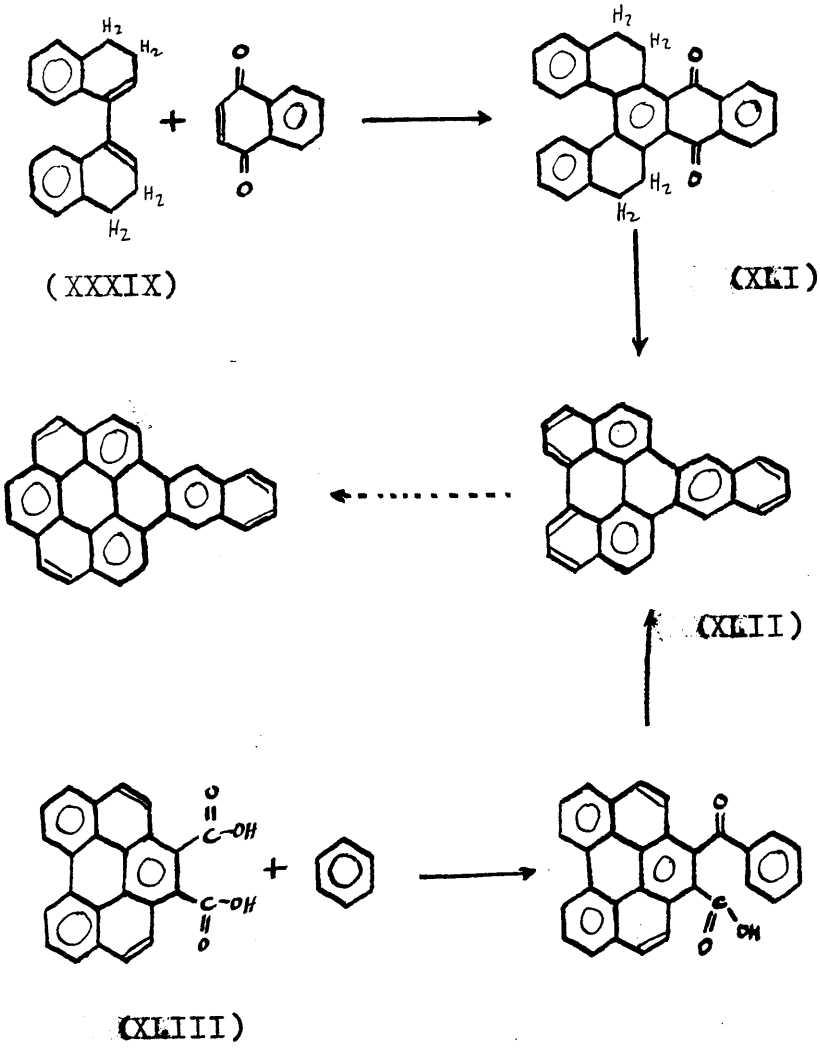
These authors added crystallographic proof of the identity of their two samples, since this could not be proved by a mixed melting point. The spectrum of their tetrabenzoperopyrene was identical with ours, though its melting point was reported as 20 degrees lower than ours.

Synthesis of 1,12-o-Phenyleneperylene (XXI) [12].

This was first attempted by a Friedel-Crafts reaction between benzene and perylene [40]. The main product was periflanthene (XXXIV) with some 3-phenylperylene (XXXV). The action of aluminium chloride on perylene and benzoquinone in nitrobenzene, followed by reduction in a zinc dust melt, gave 3,4-o-phenyleneperylene (XXXVI) and only spectroscopic traces of (XXI).

Condensation of 4,4'-dihydroxydinaphthyl and benzoquinone in boiling acetic acid and treatment of the product with aluminium chloride gave a quinone thought to be (XXXVII) [41]. Reduction by a zinc dust melt gave traces only of perylene: the quinone was probably a polymer, though it could form a vat dye.

A reference was found to the quinone (XXXVIII) [42], obtained from the diene addition of benzoquinone to



(XXXIX)

(XLI)

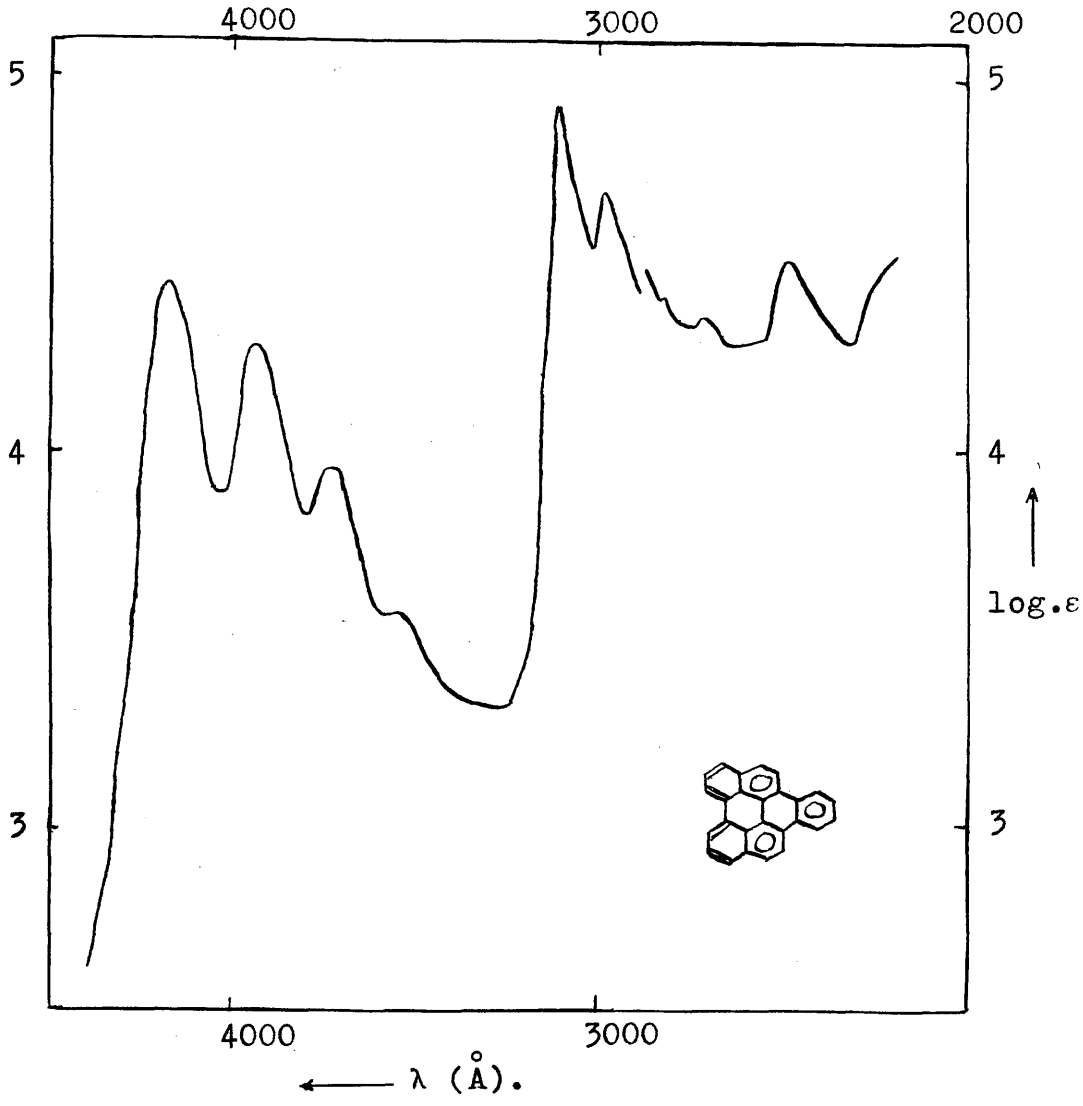
(XLII)

(XLIII)

bis-dialin (XXXIX). On reduction of this, two compounds were obtained and separated by chromatography. The first, white, compound was thought to be a hydrogenated derivative of (XXI) but was later found to be mainly dinaphthyl. The second compound crystallised from benzene in long yellow needles of 1,12-o-phenyleneperylene (XXI). Its spectrum (Fig. 3) resembled that detected in the reaction mixtures from previous attempts at synthesis. It reacted with maleic anhydride and chloranil to give an acid with the spectrum (Fig. 4) of a 1,2-benzocorpnene. This acid was therefore 1,2-benzocoronene-7,8-dicarboxylic acid (XL).

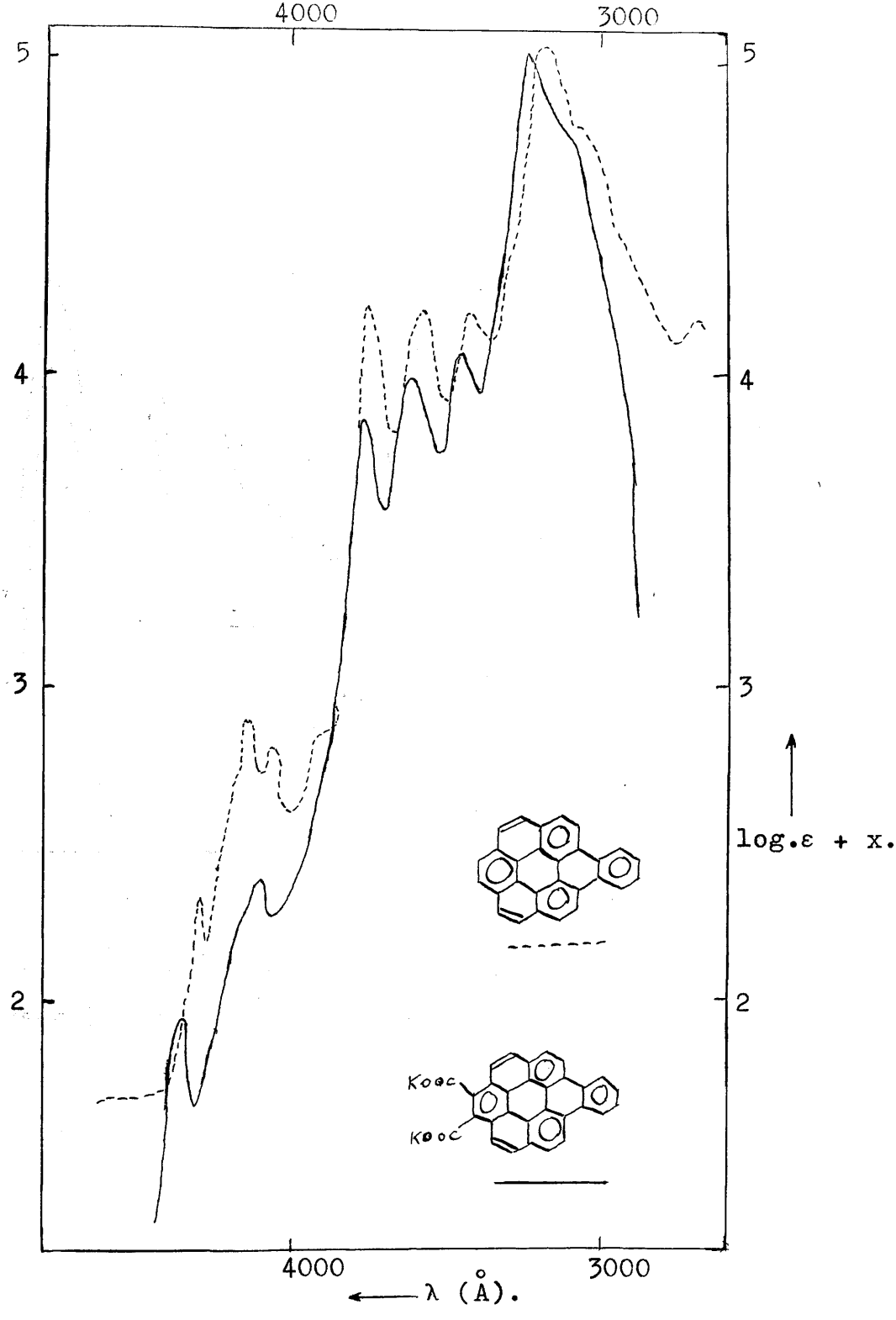
Synthesis of Dinaphtho(1',7':2,12)(1",7":3,5)-tetracene (XLII).

This compound, like (XXI), can be used for spectral studies, and possible methods of preparation are very similar. Naphthoquinone and perylene with aluminium chloride in nitrobenzene gave no result [40]. 1,4-Naphthoquinone is known to react with bis-dialin in a similar manner to benzoquinone [42], to give (XLI). Reduction of this gave the required compound (XLII), the spectrum of which (Fig. 5) is identical with that



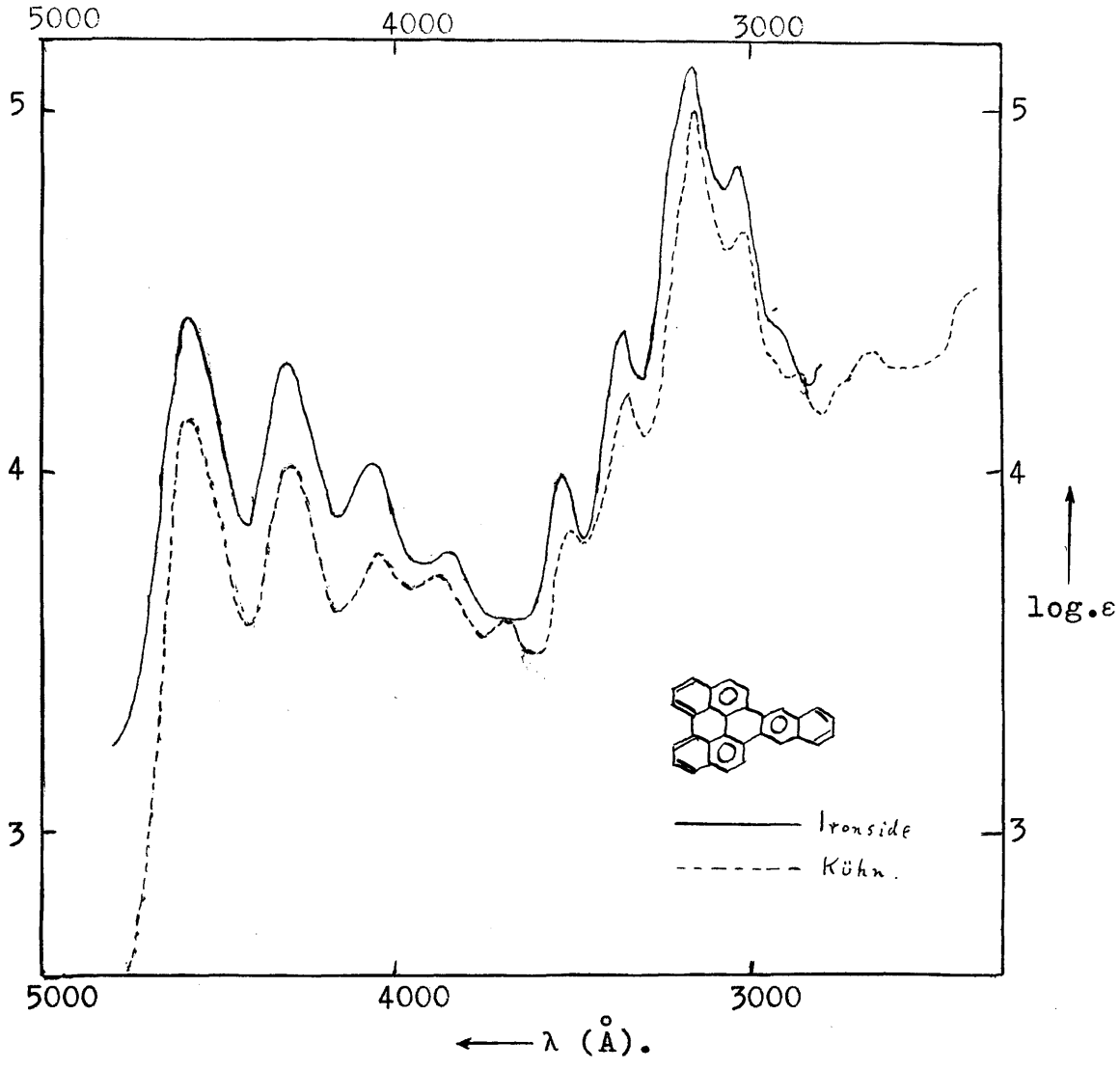
1,12-o-Phenyleneperylene (XXI), in benzene (from 2900 in cyclohexane). Absorption maxima (Å) and log.ε (in parentheses):- 4180 (4.47), 3940 (4.31), 3730 (3.97), 3530 (3.58), 3105 (4.96), 2975 (4.74), 2830 (4.45), 2720 (4.40), 2490 (4.56).

Fig. 3.



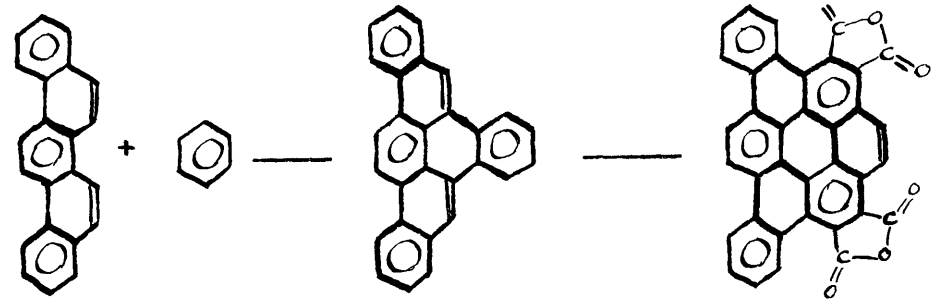
—— 1,2-Benzocoronene-7,8-dicarboxylic acid dipotassium salt, in water/ethylene glycol (50%). Absorption maxima :- 4370, 4100, 3770, 3610, 3440, 3230 Å.

Fig. 4.

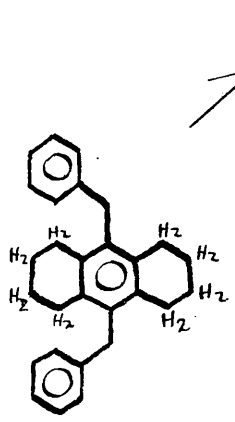


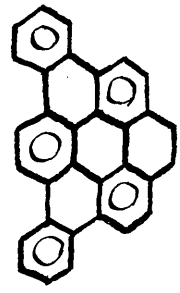
Dinaphtho(1',7':2,12)(1",7";3,5)-tetracene (XLII), in benzene (from 2900 in ethanol). Absorption maxima and log.ε :- 4575 (4.44), 4300 (4.31), 4055 (4.03), 3845 (3.78), 3520 (4.01), 3348 (4.40), 3153 (5.14), 3023 (4.86).

Fig. 5.

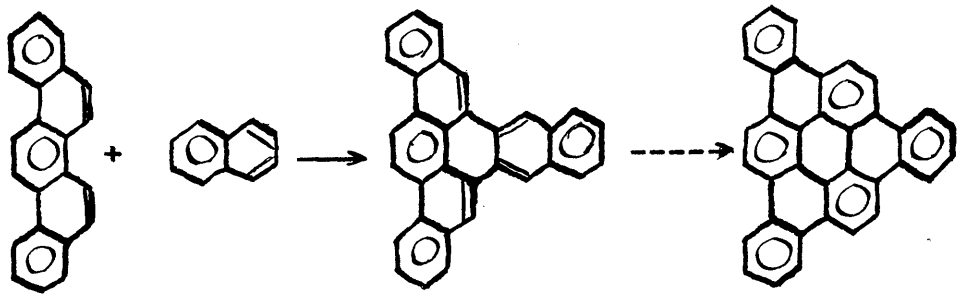


(XLV)





(XIX)



(XLIV) (XLVI)

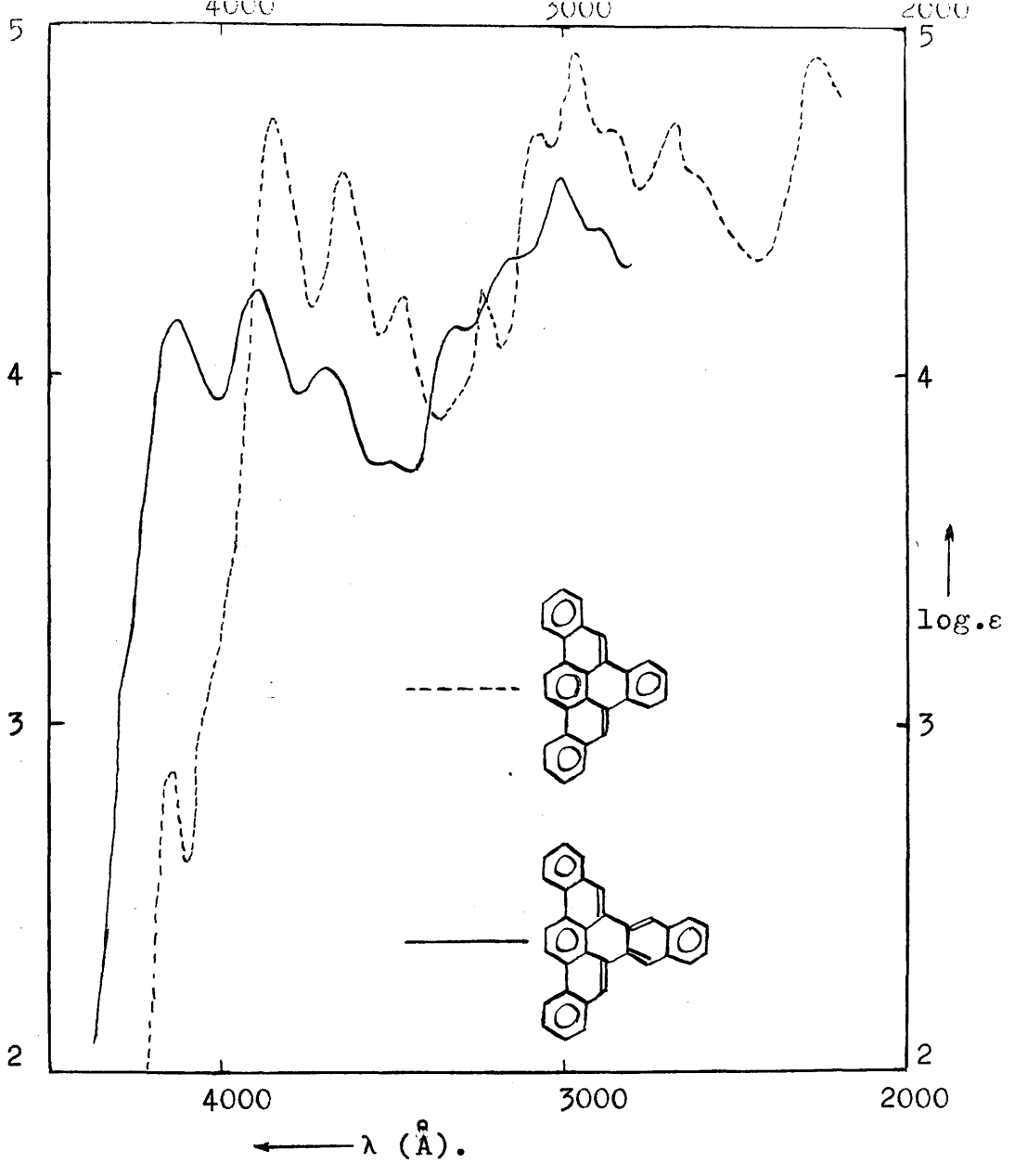
of a compound prepared in small amount from 1,12-benzoperylene-1,12-dicarboxylic acid (XLIII) and benzene under the influence of aluminium chloride [43].
This hydrocarbon dissolves in molten maleic anhydride, but so far no adduct has been isolated.

Synthesis of 4,5:8,9-Dibenzo-2',3':1,2-naphthopyrene .

Picene is reported to react with benzene in the presence of aluminium chloride to give 1,2:4,5:8,9-tribenzopyrene (XLV) [44]. This product has a different spectrum from that of the compound, also claimed to have this structure, obtained by Clar from octahydroanthracene and benzoyl chloride [45]. The first method is the more likely to be correct. The compound thus obtained reacted with maleic anhydride and chloranil and led to 1,2:5,6-dibenzocoronene (XIX), [12], which has a definitely coronene-type spectrum.

An analogous reaction of picene with naphthalene gave a compound which is taken to be 4,5:8,9-dibenzo-2',3':1,2-naphthopyrene (XLIV) . In Fig. 6 its spectrum is compared with that of tribenzopyrene prepared by the same method. Its analysis is not yet satisfactory. Reaction of (XLIV) with maleic anhydride and chloranil is expected to lead to 1,2:5,6:9,10-tribenzocoronene (XLVI).

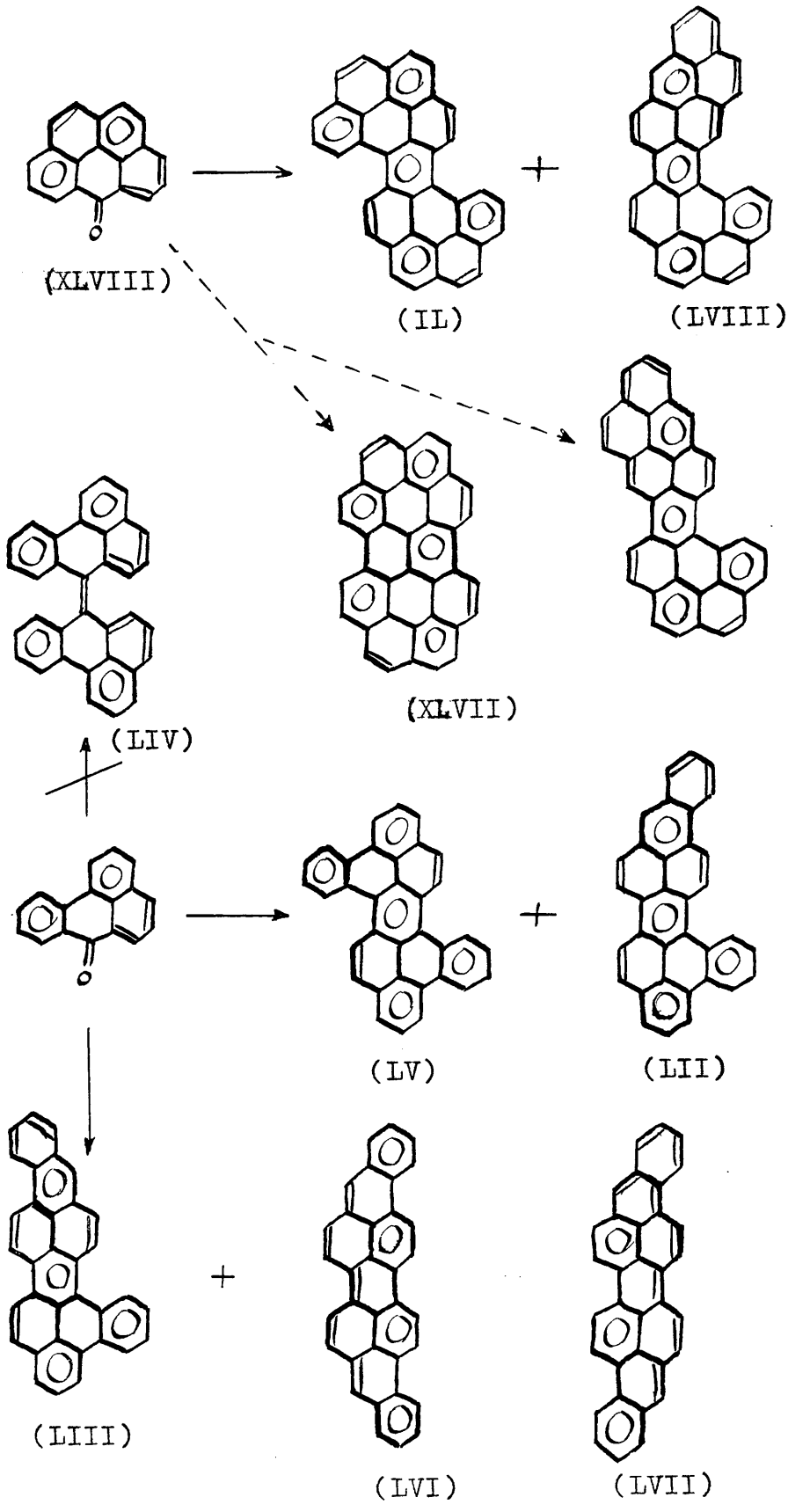
Sufficient material for this synthesis is not yet available, but preliminary trial shows that (XLIV) does react in this way. Tribenzocoronene is required for further studies of the spectra of the benzocoronenes.



—— 4,5:8,9-Dibenzo-2',3':1,2-naphthopyrene (XLIV), in benzene. Absorption maxima (Å) and log.ε :- 4135 (4.17), 3900 (4.26), 3695 (4.04), 3510 (3.76), 3325 (4.14), 3165 (4.35), 3010 (4.59), 2895 (4.44).

---- 1,2:4,5:8,9-Tribenzopyrene (XLV), in cyclohexane. Absorption maxima (Å) :- 3850, 3640, 3465, 3230, 3070, 2965, 2850, 2680, 2500, 2250.

Fig. 6.


(XLVIII)
(IL)
(LVIII)
(XLVII)
(LIV)
(LV)
(LII)
(LIII)
(LVI)
(LVII)

Attempted Syntheses of Circodiphenyl (XLVII).

Circodiphenyl (XLVII) can be considered to be a coronene derivative and would be useful for further studies of spectral changes. It could also be compared with other highly condensed hydrocarbons, such as circumanthracene (LX).

The first approach was bimolecular condensation of (2',7':1,8)-naphthanthrone (XLVIII). The preparation of this [60] was modified by the addition of the pyrene in nitrobenzene solution to the glycerol/ sulphuric acid mixture. The nitrobenzene served as a more efficient oxidising agent than air (four atoms of hydrogen require to be removed) and gave better contact between the reagents, since pyrene is immiscible with the glycerol/sulphuric acid.

Naphthanthrone was reduced in a dry melt of zinc dust and zinc chloride (when water is absent, hydrogen is not available to replace the oxygen, and bimolecular condensation occurs). The resulting mixture was separated by chromatography, but elution was so slow that this route was abandoned after two pure compounds were obtained, dinaphtho(7',1':1,13) (1",7":6,8)-peropyrene (IL), identical with a sample prepared by Kelly [46], and an isomer of indeterminate

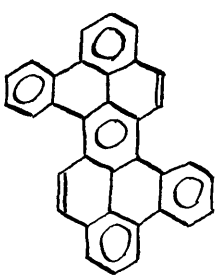
structure, (A). Fractional crystallisation of the mixture was not successful. At least two more products were thought to be present.

The same condensation was then carried out on mesobenzanthrone [47]. The products, having lower molecular weights than those from naphthanthrone, should be more easily separable, and two of the possible products, 3,4:11,12-dibenzobisanthene (L) and 3,4:10,11-dibenzobisanthene (LI) could lead to circodiphenyl if they react with maleic anhydride. Only two of the other possible products are unknown, 1,2:11,12-dibenzoperopyrene (LII) and 1,2:6,7-dibenzoperopyrene (LIII). Comparison with these would help to elucidate the structure of (A). This condensation was also carried out with phosphorous oxychloride, which was reported to give 7,7'-dibenzanthrylidene (LIV) [48]. These two methods gave the same products except that phosphorous oxychloride gave one compound more (C).

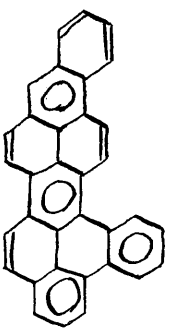
Neither of the dibenzobisanthenes was formed, nor was dibenzanthrylidene . The known 4,5:11,12-dibenzoperopyrene (LV) [49] was obtained in large amount. Two new isomers of this, absorbing at 472mμ (B) and 482mμ (C) respectively, were separated, and the final

Table 4.

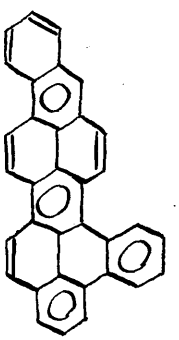
Hydrocarbon	λ_p (Å), $\sqrt{\lambda_p}$		Difference from peropyrene.($\sqrt{Å}$).
Peropyrene	4440	66.64	
(LV)	4450	66.71	0.07
Violanthrene (LVI)	4920	70.15	3.51
Isoviolanthrene (LVII)	5150	71.76	5.12
(B)	4720	68.70	2.06
(LII) calculated.	4684	68.43	$\frac{3.51 + 0.07}{2}$
(C)	4820	69.42	2.78
(LIII) calculated.	4793	69.23	$\frac{5.12 + 0.07}{2}$



(LV)



(LII)



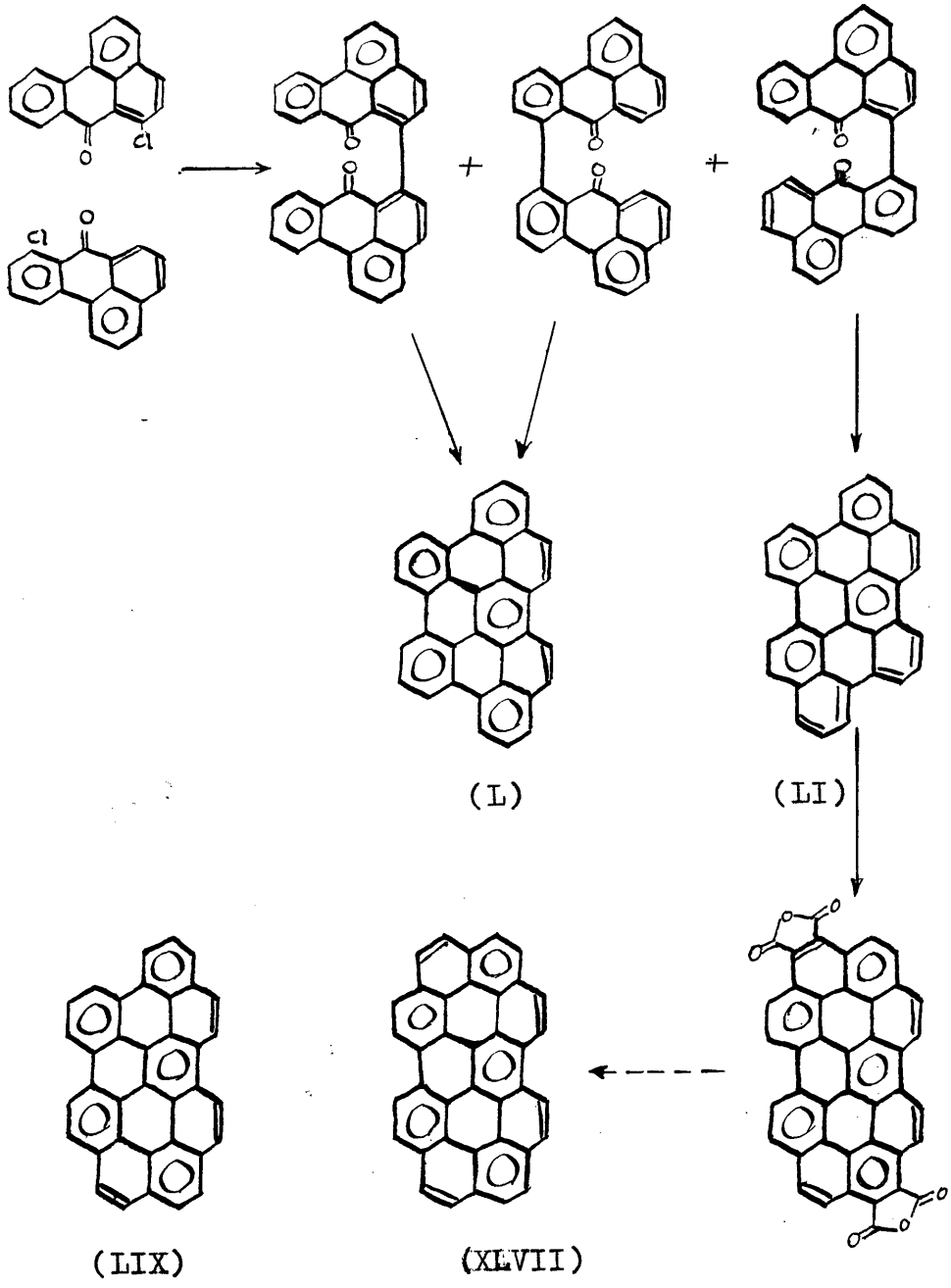
(LIII)

product was violanthrene (LVI). Only spectroscopic traces of isoviolanthrene (LVII) were found, as in the condensation of benzanthrone in an alkali melt [50]. Separation was achieved most easily by fractional extraction and crystallisation.

Comparison of the spectral shifts for the addition of two benzo- groups tp the different positions of peropyrene is made in Table 4. In this case, the p-bands are suitable for comparison, since the isomers can all have similar excited states to peropyrene itself, which is excited in the 1,8 or 1,10 positions [51]. Addition of a ring in the 4,5- or 11,12- positions brings little change. Rings in the 1,2-, 2,3-, 8,9-, or 9,10- positions cause larger shifts, which appear to be smallest when both added rings are on the same side of the molecule. Hence (B), which absorbs nearer the violet than (C), is 1,2:11,12-dibenzoperopyrene (LII) and (C) is 1,2:6,7-dibenzoperopyrene (LIII).

Since (LII),(B), comes second from a chromatogram, after (LV), (A) probably corresponds to it and is dinaphtho(7',1':1,13)(1",7":9,11)-peropyrene (LVIII).

The two dibenzbisanthenes still remained unknown. One of these (L), is reported to be formed in minute yield by reduction of benzanthrone in a melt of zinc dust and aluminium chloride [49].

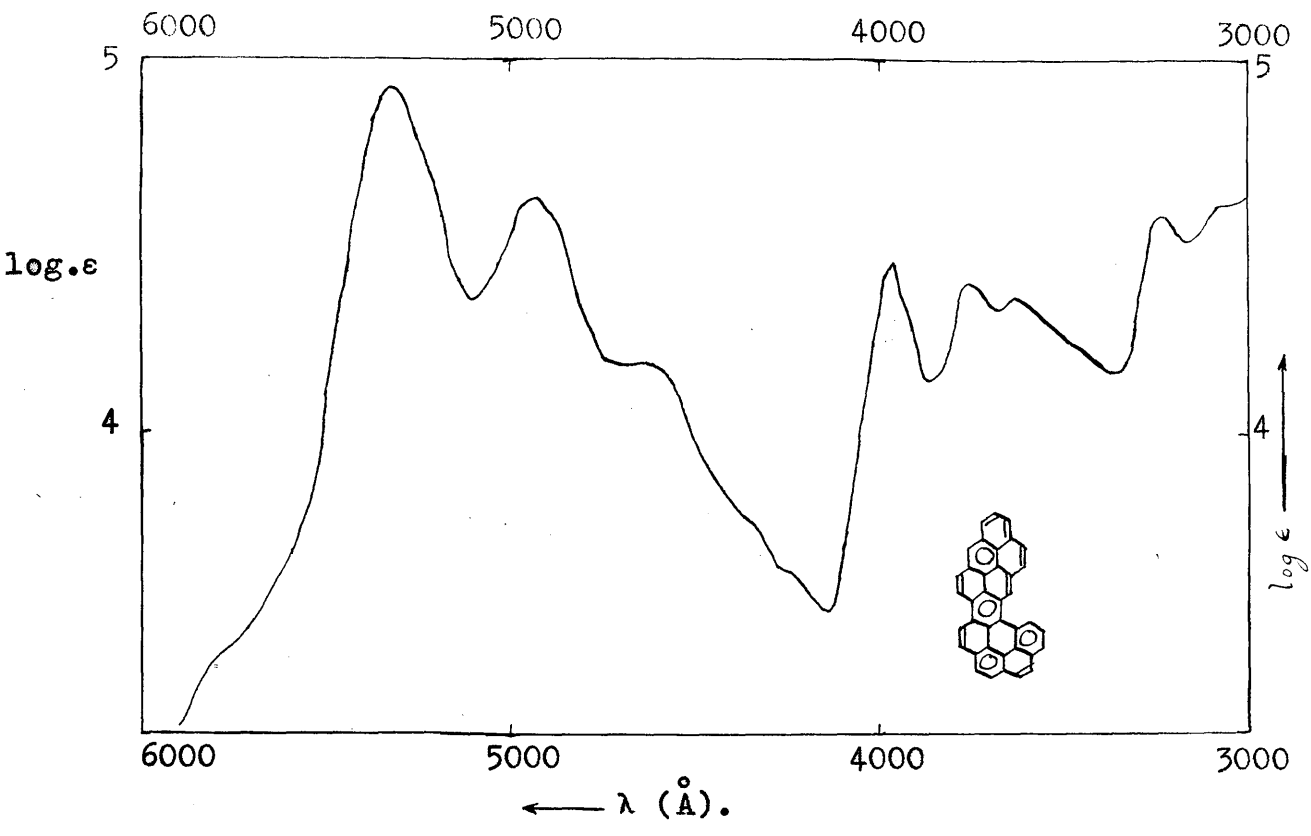

Cl
O
Cl
O
+
+
(L)
(LI)
(LIX)
(XLVII)

A better route seems to be reductive condensation of 6,6'-dimesobenzanthronyl [52], though this has already been tried without success, using aluminium powder in concentrated sulphuric acid, zinc and hydrochloric acid, and sodium amalgam with pyridine and a little water [52]. A dry zinc dust melt should achieve this condensation as easily as that of benzanthrone.

Preparation of chlorobenzanthrone gave 8-chlorobenzanthrone and a eutectic mixture of this with 6-chlorobenzanthrone [53]. Bimolecular coupling of the former with copper powder [52], followed by reduction in a zinc dust melt, gave 3,4:11,12-dibenzobisanthene (L). Only one compound was formed and there was no sign of rearrangement occurring during reduction. Similar treatment of the eutectic mixture gave a mixture of (L) and 3,4:10,11-dibenzobisanthene (LI), due to formation of 6,8'-dibenzanthronyl, since both 6,6'- and 8,8'-dibenzanthronyl should give (L). This mixture could not be separated by crystallisation or chromatography, so the spectrum of (LI) was obtained by subtraction. The spectra of the new compounds obtained in these attempts to prepare circodiphenyl are given in Figs. 7 to 11.

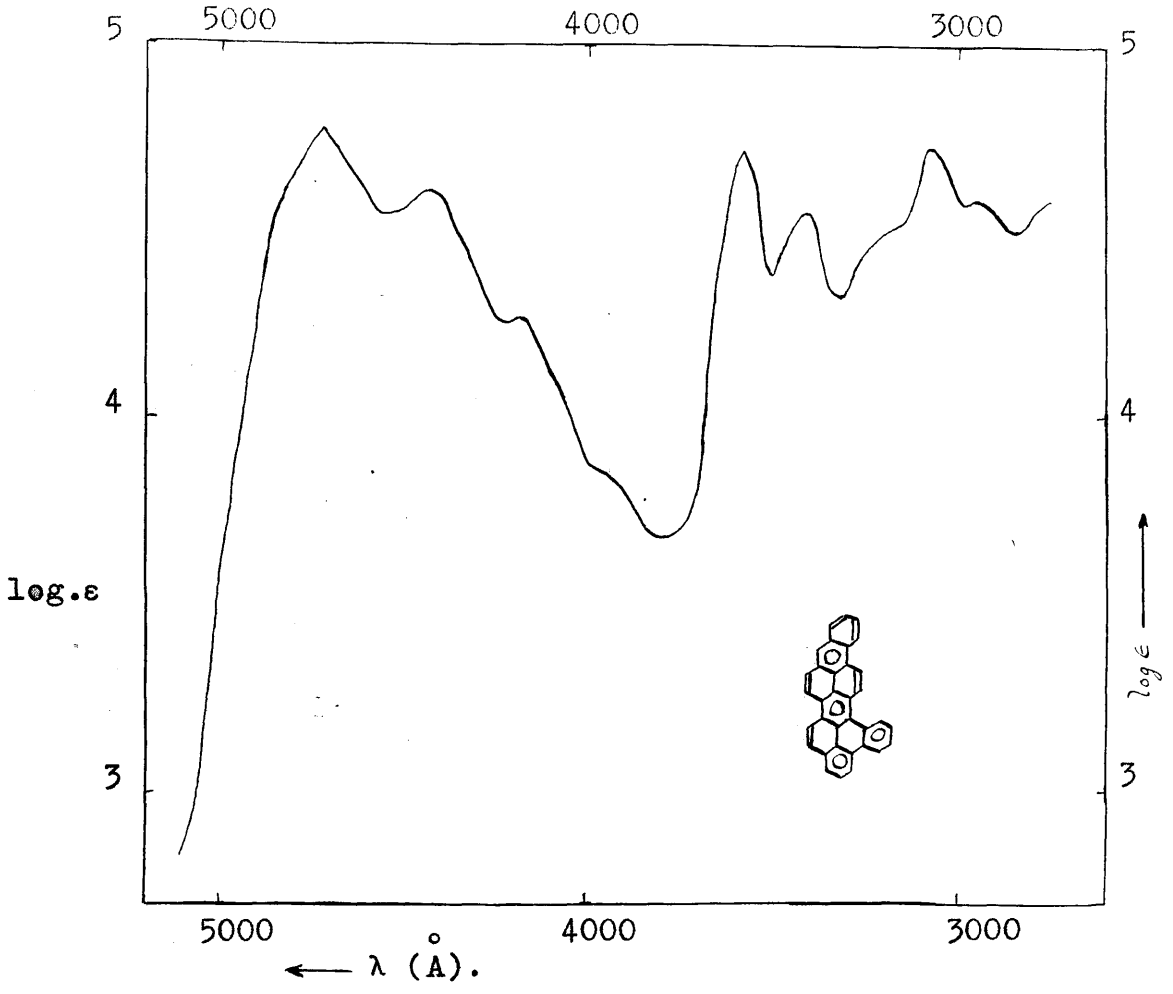
(LI) reacted much more readily than its isomer (L) with maleic anhydride; the mixture of (L) and (LI) was treated with maleic anhydride and chloranil,

the adduct was extracted with alkali, reprecipitated and decarboxylated with soda-lime. The product was mainly (L), formed by splitting of the tetra-acid, though this isomer reacted with more difficulty than (LI), together with a very small amount of a new compound, thought to be circodiphenyl rather than the product of mono-addition (LIX); but too little material was available for separation.



Dinaphtho(7',1':1,13)(1",7":9,11)-peropyrene (LVIII), in benzene. Absorption maxima (Å) and log.ε (in parentheses):- 5330 (4.93), 4950 (4.64), 4650 (4.20), 3960 (4.48), 3760 (4.42), 3630 (4.37), 3240 (4.60).

Fig. 7.

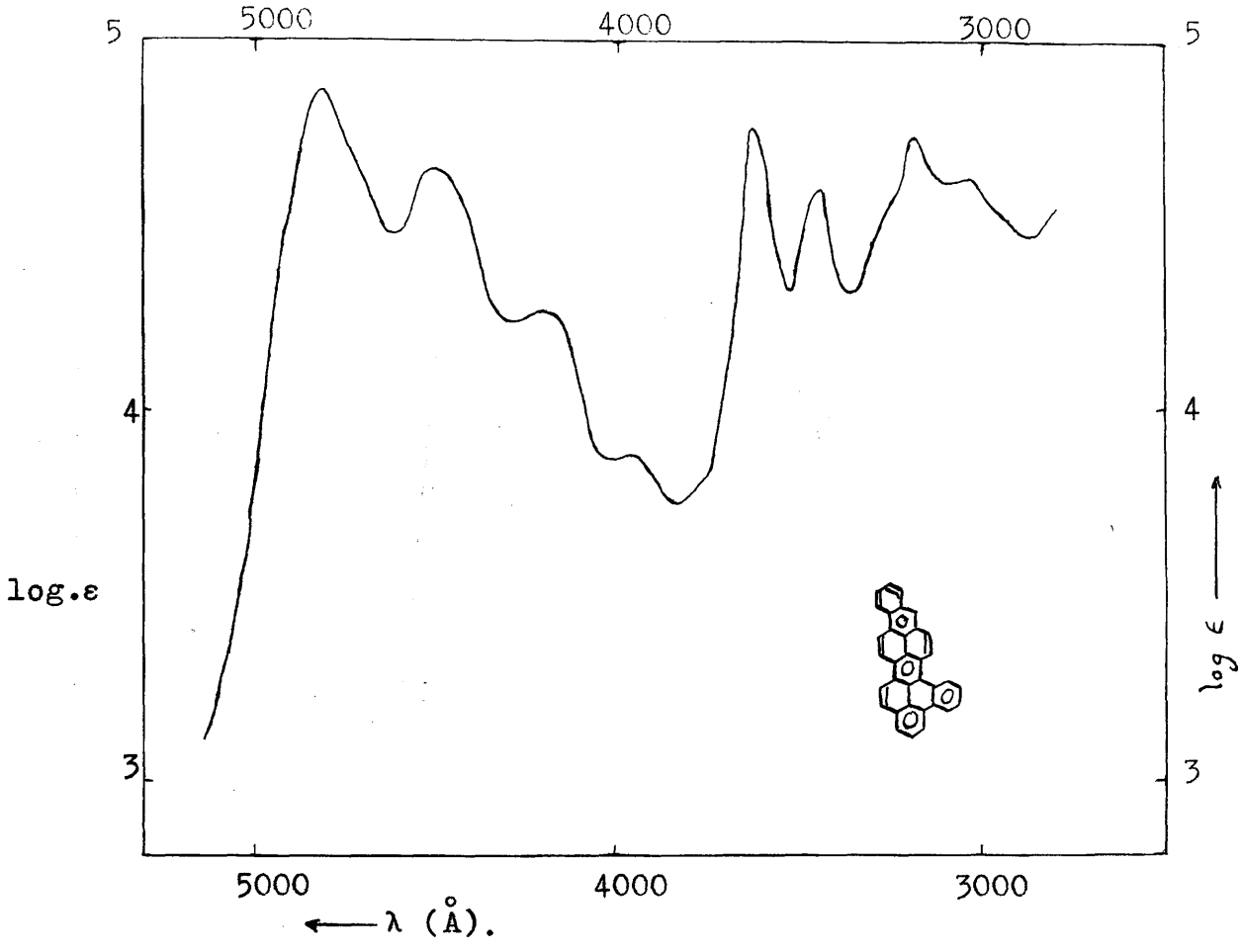


1,2:11,12-Dibenzoperopyrene (LII) in benzene.

Absorption maxima (Å) and log.ε (in parentheses) :-

4720, 4450, 4180, 3580,3415, 3070, 2950.
(4.78)(4.62)(4.27)(4.72)(4.55)(4.73)(4.59).

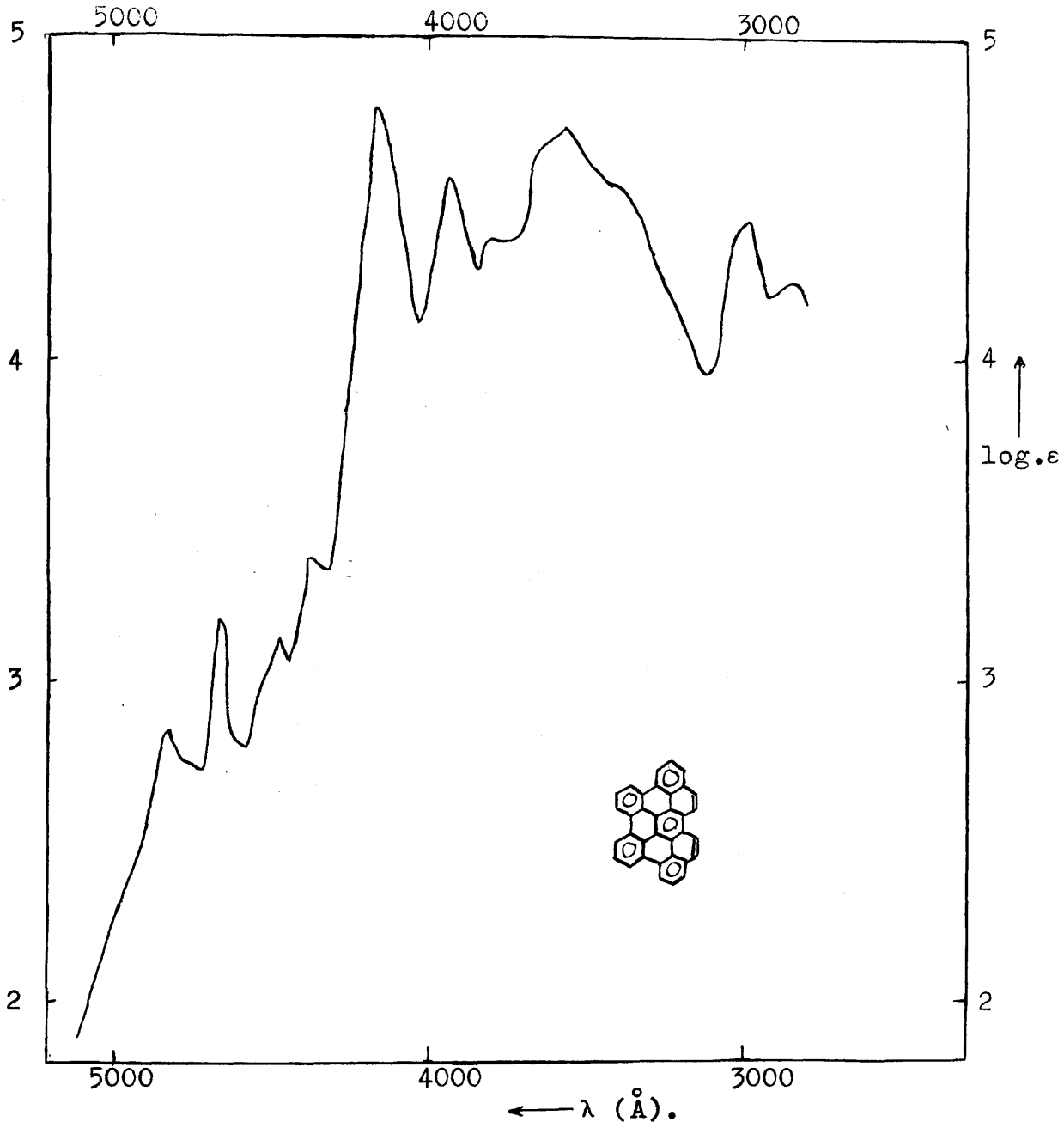
Fig. 8.



1,2:6,7-Dibenzoperopyrene (LIII), in benzene.
Absorption maxima (Å) and log.ε (in parentheses):-

4820 (4.87), 4530(4.66), 4200 (4.28), 3960 (3.89),
3630 (4.78), 3460 (4.61), 3185 (4.75), 3060 (4.63).

Fig. 9.

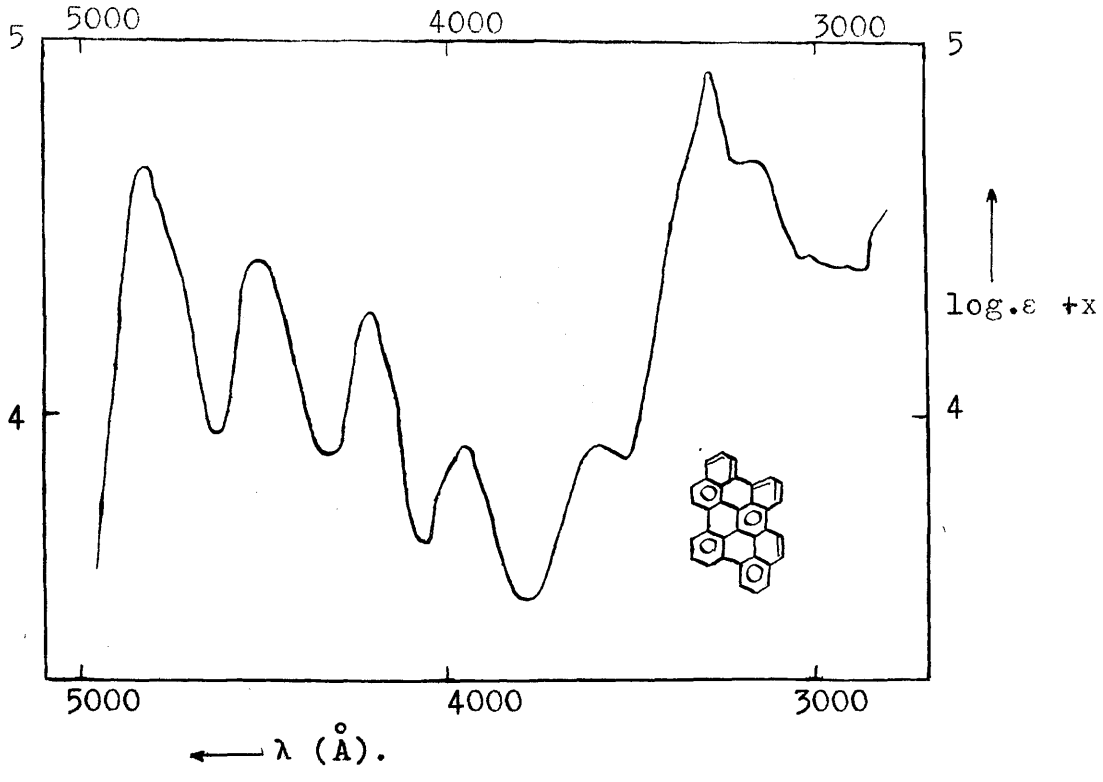


3,4:11,12-Dibenzobisanthene (L), in benzene.

Absorption maxima (Å) and log.ε (in parentheses):-

4820 (2.85), 4660 (3.20), 4475 (3.13), 4380 (3.39), 4170 (4.80), 3945 (4.58), 3810 (4.40), 3580 (4.73), 2995 (4.45), 2850 (4.25).

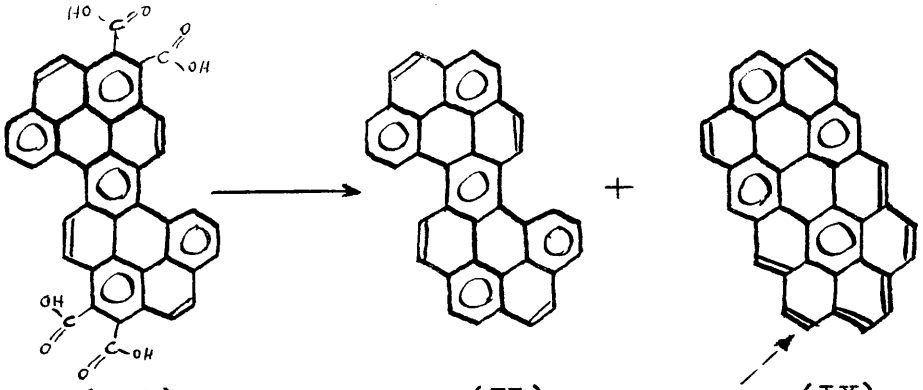
Fig.10.



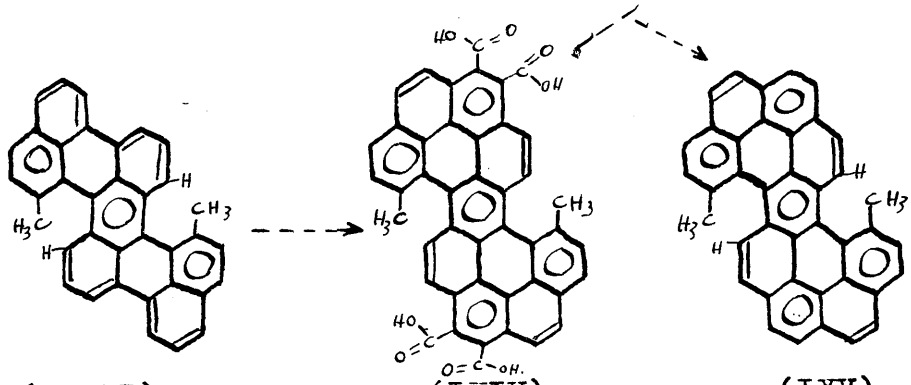
3,4:10,11-Dibenzobisanthene (LI), in benzene.
Absorption maxima (Å) :- 4820, 4510, 4200, 3940, 3580, 3290, 3160, 3000.

Fig. 11.

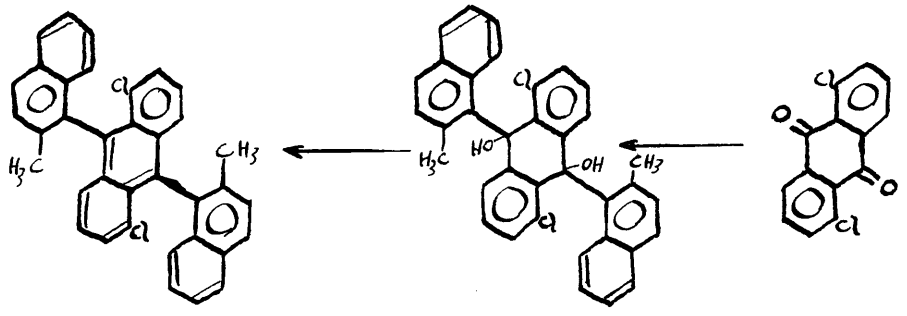
51.



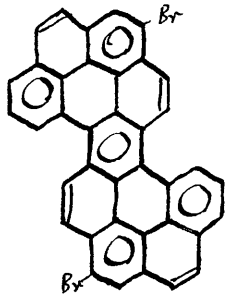
(LXI) (IL) (LX)



(LXIII) (LXIV) (LXV)



(LXVII) (LXVI)



(LXII).

Attempted Syntheses of Circumanthracene (LX).

Circumanthracene is an interesting, highly condensed hydrocarbon, first prepared as a by-product in the preparation of dinaphtho(7',1':1,13)(1",7":6,8)-peropyrene (IL) from its tetracarboxylic acid (LXI) [46], and it is therefore produced from one of these two compounds. Its structure was suggested by its properties and proved by X-ray diffraction analysis. This is the first compound known to be produced by formation of a new aromatic ring through addition of one carbon atom to five others. The usual methods are two plus four or three plus three, carbon atoms.

The two single carbon atoms added, may have come either from the carboxyl groups of the acid, or from partial decomposition of the hydrocarbon. The use of radioactive carbon in the carboxyl groups has given no clear decision [54].

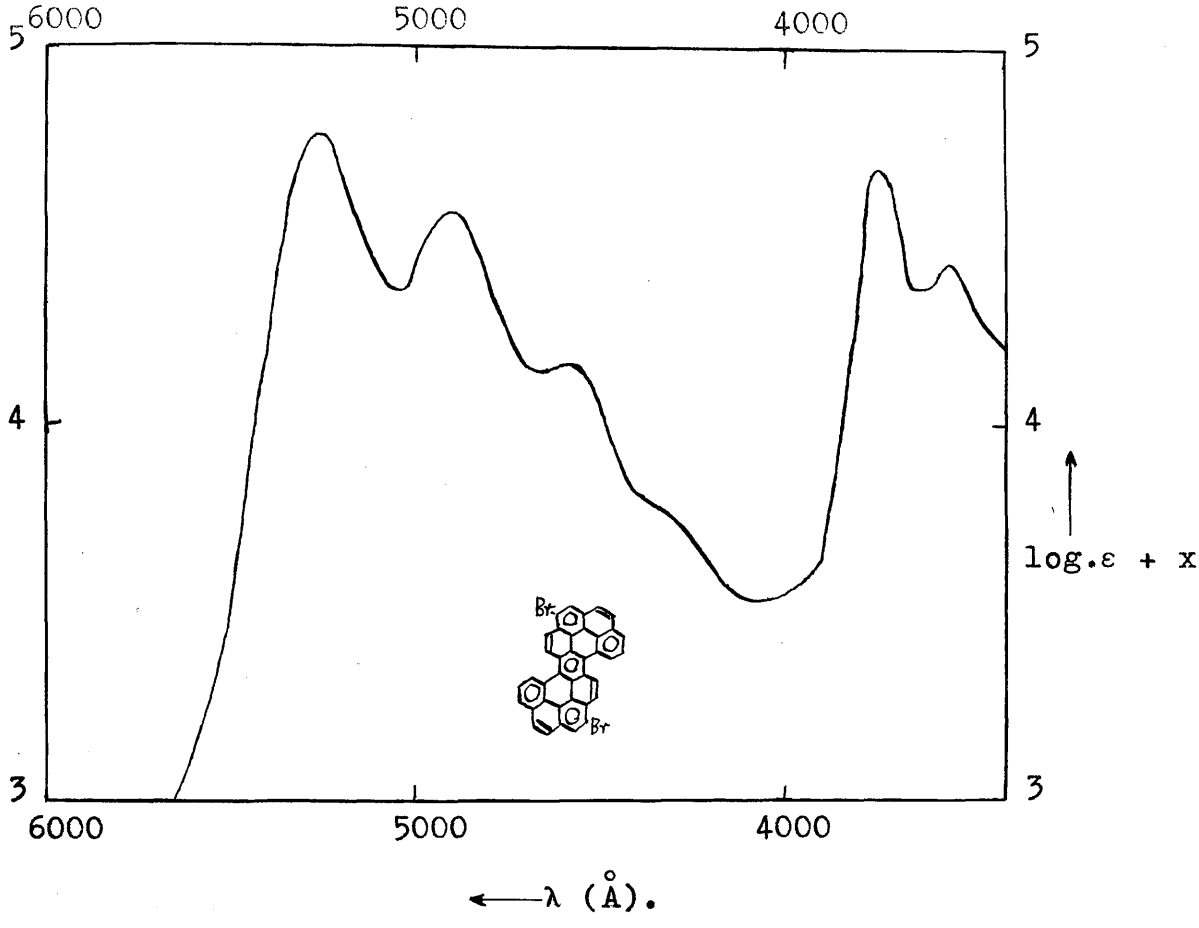
Synthesis of circumanthracene was attempted by treatment of dinaphthoperopyrene (IL) or its acid, with various reagents which seemed likely to supply single carbon atoms.

Since potassium phthalate is reported to rearrange to potassium terephthalate [55], the acid (LXI) was

mixed with potassium carbonate and treated as described in this reference. Decarboxylation took place, but only a faint suggestion of circumanthracene was seen in the spectrum of the product.

Several attempts were made to supply the required carbon atoms from other reagents, maleic anhydride, bromomaleic anhydride, sodium formate, formaldehyde, dichloroacetic acid, etc. Many of these reactions gave reddish solutions in xylene, but only those between sodium formate or formaldehyde and the acid and between formaldehyde and the hydrocarbon, gave any reasonable amount of circumanthracene. In each case, the product oxidised more easily than was expected, and repetitions of the experiments were not successful, so that no circumanthracene was isolated. Under the conditions used, sodium formate decomposes to carbon monoxide and water [56]. It is also reported to give formaldehyde [57] which may thus be the actual reagent.

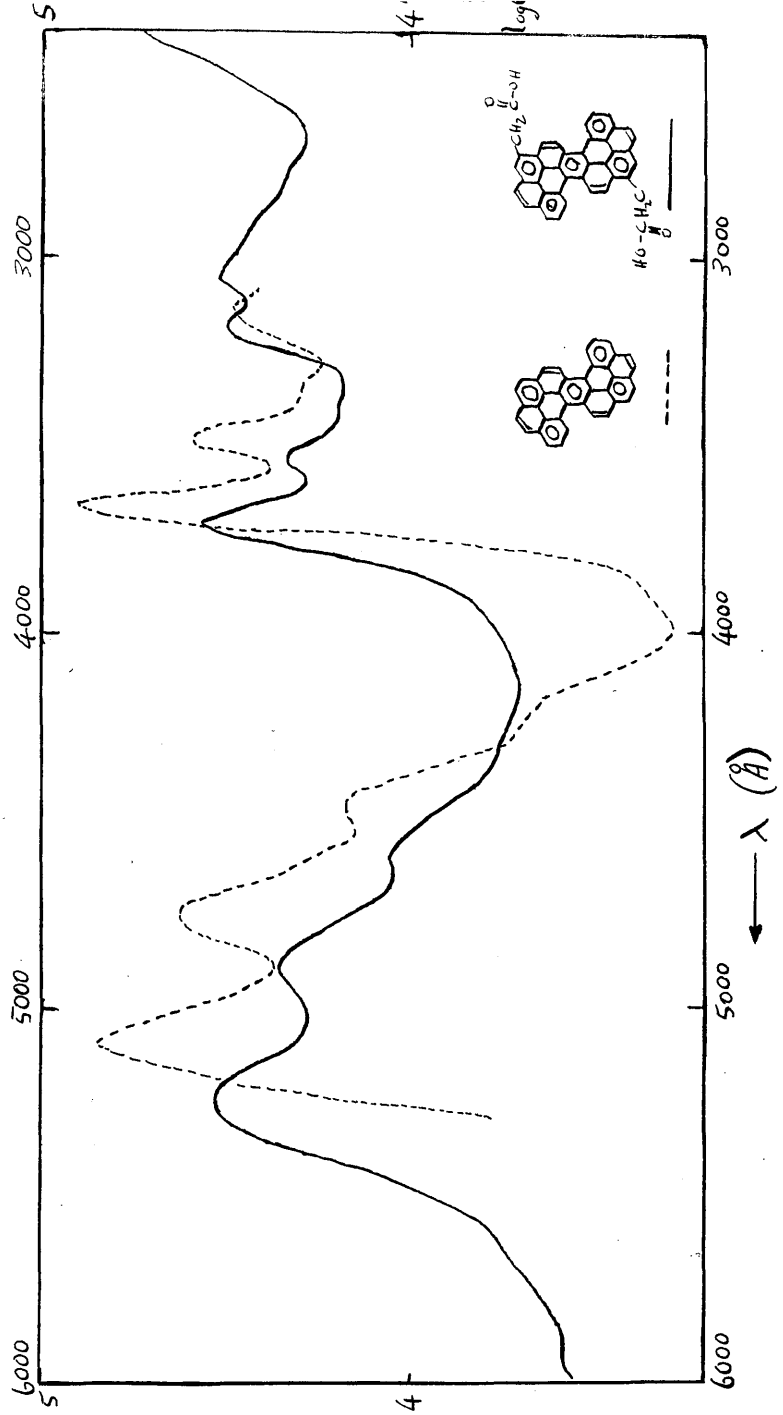
Reaction of bromomaleic anhydride on dinaphthoperopyrene gave a dibromo-compound. Its spectrum is given in Fig. 12. It is probably the 1,8-dibromo-compound since these are the reactive positions in peropyrenes.



1,8-Dibromodinaphtho-(7',1':1,13)(1",7":6,8)-peropyrene (LXII) in trichlorobenzene.

Absorption maxima:- 5270, 4920, 4600, 3760, 3560 Å.

Fig. 12.



---- Dinaphtho(7',1':1,13)(1",7":6,8)-peropyrene (IL), in benzene.

—— Acid derivative from (IL) and dichloroacetic acid, in ethanol.

Fig. 13.

Some similar reactions were tried on 4,5:11,12-dibenzoperopyrene (LV) which contains similar gaps to those in dinaphthoperopyrene (IL). All were unsuccessful. In both (LV) and (IL), addition of one carbon cannot give a fully aromatic structure; if simultaneous reaction of two separate carbons is required, the probability is very low.

Dichloroacetic acid reacted with dinaphthoperopyrene when refluxed: an acid was produced, but its spectrum (Fig. 13) showed it to be a derivative of the starting material and not of circumanthracene.

Irradiation of a cold mixture of dichloroacetic acid and dinaphthoperopyrene caused a change in spectrum, but only dinaphthoperopyrene was recovered. It was decided that in this case the product formed was two molecules of dinaphthoperopyrene linked together: sublimation split the connecting bond to give the starting material.

Addition of Maleic Anhydride to 7',7"-dimethyl-1,9L5,10-diperinaphthyleneanthracene (LXIII).

Synthesis of circumanthracene was also attempted by addition of maleic anhydride to 7',7"-dimethyl-1,9:5,10-diperinaphthyleneanthracene (LXIII) [58].

At first this addition proceeded smoothly, but the adduct dissociated to starting material on decarboxylation. Attempts to prepare more (LXIII) ran into complications.

Milder methods than those published were adopted for the final ring closure to (LXIII) from (LXVII). Later reactions failed under these conditions, and required much larger amounts of alkali. The product then obtained did not react with maleic anhydride and differed slightly in spectrum (Fig. 14) and melting point from the previous material.

This compound (LXIII), may possibly exist in optical isomers, due to the overcrowded methyl groups. The difficult alkali fusion suggests that the new isomer is the d,l one, since the meso form will have a more stable propeller-like shape. Coulson has shown that this shape is the more stable for tetrabenzo-peropyrene (IX) which is similarly strained [39].

The chloro-compound (LXVII) must have the same configuration as the hydrocarbon (LXIII). The diol (LXVI) can also exist in d,l and meso forms: it is not obvious which of these corresponds to the isomers of the later compounds. Isomerism in (LXIII) is therefore determined in the initial Grignard reaction, or possibly in reduction of the diol (LXVI).

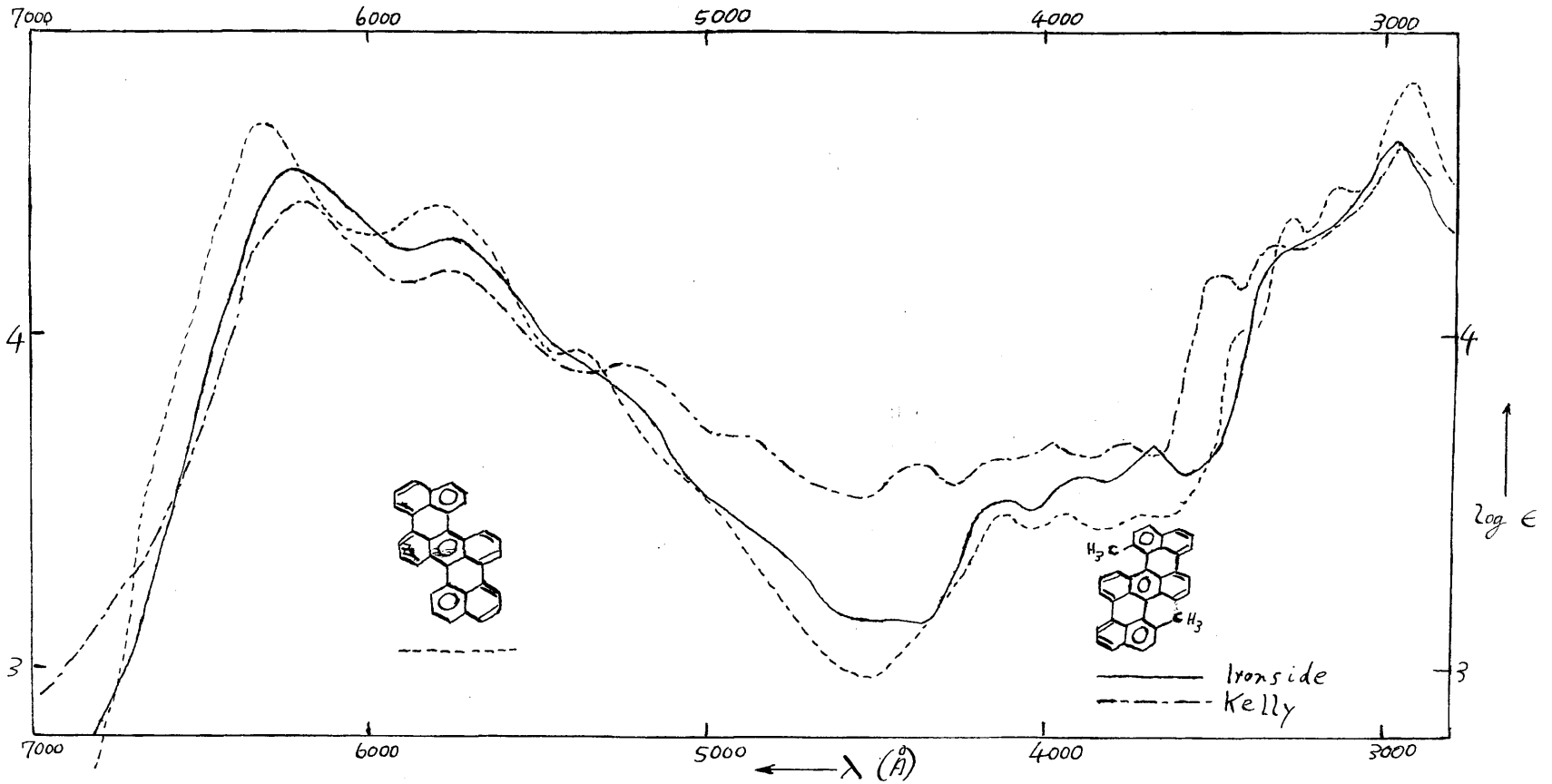


Fig. 14.

7',7''-Dimethyl-1,9:5,10-diperinaphthylene anthracene (LXIII), in benzene.

Maxima (Å):— Ironside : 6250, 5760, 5 4460, 4100, 3870, 3680, 2970

Kelly : 6210, 5780, 5250, 4390, 3980, 3780, 3510, 3320, 2960.

EXPERIMENTAL.

E X P E R I M E N T A L.

(All melting points are uncorrected and were taken in evacuated capillaries. Microanalyses are by Mr. J.M.L. Cameron and his staff).

Synthesis of Hexabenzocoronene [10),34)].

1,9:2,3-Dibenzanthrene Perbromide.- Bromine (7.5g., 5 atoms) in dry benzene (20ml.) was added to a solution of dibenzanthrene (XXIX) in benzene (100ml.). There was an immediate precipitate of the dark brown perbromide, which was filtered off, washed with benzene and dried in a vacuum at 50°C (yield 7.9g., theoretical is 9.6g. but some hydrogen bromide came off during drying). (Found: C, 50.8; H, 2.8; Br, 46.8. $C_{21}H_{14}Br_3$ requires C, 49.8; H, 2.8; Br, 47.4%). It decomposed slowly at room temperature with evolution of hydrogen bromide. It dissolved, when warmed, in aqueous acetone, and on cooling, needles of dibenzanthrene (XXIX), m.p. 170°, crystallised out. In boiling acetic acid, the perbromide formed a mixture of dibenzanthrone (XXVIII), m.p. 208°, and dibenzanthrene, which were separated by crystallisation from xylene and acetic acid. The perbromide melted

at 153° with evolution of hydrogen bromide, and resolidified immediately to a solid with a vivid green surface shine, which contained tetrabenzoperopyrene (IX). The perbromide gave up bromine when a suspension in nitrobenzene or carbon disulphide was titrated with aqueous sodium thiosulphate (potassium iodide-starch indicator) (Found: 1.6 atoms of bromine/molecule in nitrobenzene; 1.8 in carbon disulphide).

Microwave absorption showed that the perbromide was not paramagnetic [59]. A similar adduct of one atom of bromine and one molecule of mesobenzanthrone [36] also gave a negative result.

4,5:6,7:11,12:13,14-Tetrabenzoperopyrene (IX).- (a) Dibenzanthrene perbromide (3.15g.) was melted in a vacuum at 153° (Found: loss, 1.38g. Calc. for 3HBr: 1.51g.). The powdered melt was sublimed first at 400°/0.1mm. then at 500°; tetrabenzoperopyrene sublimed in orange prisms, mixed with hexabenzocoronene. Extraction with 1,2,4-trichlorobenzene removed all the tetrabenzoperopyrene, which was recovered with difficulty from this solvent (yield 0.55g.). Crystallisation from xylene gave small orange prisms (Found: C, 96.0; H, 4.1. $C_{42}H_{22}$

requires C, 95.8; H, 4.2%). It did not dissolve in cold concentrated sulphuric acid, melted at 481-482° with evolution of hydrogen (86% of the calculated volume for loss of $2H_2$ was collected), and resolidified with formation of hexabenzocoronene (V). In solid solution in dioxan at -180°C. it showed orange phosphorescence of very long life, when irradiated with a mercury lamp.

(b) Dibenzanthrene perbromide (4.3g.) was refluxed in trichlorobenzene. Much hydrogen bromide and a little bromine were given off. This produced tetrabenzoperopyrene (1.05g.) and no hexabenzocoronene.

1,12:2,3:4,5:6,7:8,9:10,11-Hexabenzocoronene (V).

(a) The crude molten tetrabenzoperopyrene was sublimed at 500°/0.1mm. Hexabenzocoronene sublimed in brownish-yellow needles which were recrystallised from boiling pyrene at about 390°, under carbon dioxide. When the pyrene was on the point of solidifying, hot 1-methylnaphthalene was added to dissolve it. This gave long flat needles of hexabenzocoronene which were resublimed (Found: C, 96.4; H, 3.5. $C_{42}H_{18}$ requires C, 96.5; H, 3.5%). This compound was insoluble in concentrated sulphuric acid, and

only slightly soluble in trichlorobenzene, in which it showed strong orange phosphorescence of long life when cooled to -180° and irradiated with a mercury lamp. The short-life blue phosphorescence of trichlorobenzene was easily masked by it. It did not melt at 700°C. Its analysis was difficult because of its extreme stability.

(b) The residue from the Elbs reaction for the preparation of dibenzanthrene [37] was extracted twice with xylene and 1-methylnaphthylene, washed with benzene, dried and powdered (31.1g.). The extracts contained nothing useful. Sublimation of the residue at 480°/0.1mm. and crystallisation from boiling pyrene gave hexabenzocoronene (about 1g.), identical with the previous sample.

(c) Dibenzanthrene (2.6g.) was powdered with sulphur (0.64g.; 2 atomic proportions). The mixture was melted at 220° with evolution of hydrogen sulphide, and resolidified. After extraction with xylene the residue was sublimed from copper powder at 500°/0.1 mm. and recrystallised. The hydrocarbon was again identical with previous samples. The yield was very variable.

Synthesis of 1,12-o-Phenyleneperylene (XXI) [12].

The quinone (XXXVIII) [42] (0.6 g.) was ground up with zinc dust (1.5 g.) and sodium chloride (1.5 g.) and was melted with zinc chloride (7.5 g.) and a few drops of water, with constant stirring. When the foaming subsided, the temperature was raised to 310° at which it was kept for 10 minutes. The colour changed to bright yellow. On extraction with benzene, some crystals of 1,12-o-phenyleneperylene were obtained. It was purified by chromatography on alumina to remove perylene and 1,1'-dinaphthyl. Possibly a hydrogenated derivative of o-phenyleneperylene was also present, but it was very hard to separate from dinaphthyl. 1,12-o-phenyleneperylene (XXI) crystallised from benzene in long yellow needles, m.p. 268-270°C. (Found: C, 95.9; H, 4.3. $C_{26}H_{14}$ requires C, 95.7; H, 4.3%).

o-Phenyleneperylene reacted readily with boiling maleic anhydride and chloranil to form the red-brown anhydride of 1,2-benzocoronene-7,8-dicarboxylic acid (XL).

Synthesis of Dinaphtho(1',7':2,12)(1",7":3,5)-tetracene (XLII).

The quinone (XLI) was prepared as described [42],

with the modification that nitrobenzene was added to the reaction mixture and was distilled off after completion of the reaction.

The quinone (XLI) (2.0 g.) was fused with sodium chloride (4.0 g.) and zinc chloride (20 g.), and was kept at 300° for 8 minutes, with constant stirring. The product was washed in the normal manner, to remove inorganic salts, was dried and sublimed at 360°/0.1mm. It gave a small quantity of 1,1'-dinaphthyl and a larger amount of a dark red solid. The red impurity could not be removed by crystallisation, but chromatography on alumina gave three pure fractions:- light yellow needles readily soluble in benzene and having absorption bands at 438 and 428 mμ; secondly, yellow needles of dinaphtho(1',7':2,12)(1",7":3,5)-tetracene (XLII), which melted at 356°C., were moderately soluble in benzene and dissolved slowly in cold concentrated sulphuric acid, with a green colour.(Found: C, 95.5; H, 4.1. $C_{30}H_{16}$ requires C, 95.7; H, 4.3%). The spectrum of this compound was identical with that found by Kühn [43]. The third compound from the chromatogram formed red needles and appeared to contain oxygen.
When this zinc chloride melt was repeated with the addition of zinc dust, none of the red byproduct was formed.

Synthesis of 4,5:8,9-Dibenzo-2',3':1,2-naphthopyrene.

Picene (5.0 g.) and naphthalene (5.0 g.) were refluxed in chlorobenzene (100ml.) with powdered aluminium chloride (10g.) and stannic chloride (12g.), on a steam bath. The colour soon changed from reddish brown to green. After 3 hours the colour was blue. The product was worked up in the usual manner, and sublimed to separate unreacted picene and naphthalene. Chromatography on alumina gave a large fraction of yellow 4,5:8,9-dibenzo-2',3':1,2-naphthopyrene (XLIV). This compound gave a good spectrum, but analysis is not yet correct for the postulated structure.

Attempted Syntheses of Circodiphenyl (XLVII).

2',7':1,8-Naphthanthrone:- The method in the literature [60] was modified by dissolving the pyrene in two moles of nitrobenzene and raising this solution to 100° before adding it to the glycerol/sulphuric acid mixture at 100°. The yield was 31% after crystallisation from xylene.

Reductive Condensation of Naphthanthrone:-

Naphthanthrone (5g.) was ground up with zinc dust (5g.), sodium chloride (5g.) and zinc chloride (25g.). The mixture was melted and kept at 330° for 5 minutes, with constant stirring. The colour changed from yellow to red and then to brownish red, and traces of red sublimate were seen. There was no frothing, since this reduction was done in the absence of water, to cause bimolecular condensation. The product was washed as usual, and byproducts of low molecular weight were removed by extraction with petroleum ether (60-80°).

The crude product was extracted with xylene in a Soxhlet: crystallisation from xylene gave poor separation, so the mixture (11,9g.) was chromatographed on alumina. A large amount (3.55g.) of dinaphtho-(7',1':1,13)(1",7":6,8)-peropyrene (IL), identical

with a sample prepared by Kelly [46] was first obtained. After some mixed material came a pure solution which gave reddish brown crystals of dinaphtho(7',1':1,13)(1",7":9,11)-peropyrene (LVIII), (0.4 g.),m.p. 358-360°C. (Found: C, 96.3; H, 3.8. $C_{38}H_{18}$ requires C, 96.2; H, 3.8%). This compound gave a dark green colour in concentrated sulphuric acid.

The later stages of this chromatogram were eluted with hot xylene, but the elute became so dilute that efforts to obtain further products had to be abandoned.

Condensation of Mesobenzanthrone.

(a) Condensation with Phosphorus Oxychloride [47),48)]:-

The condensation was carried out by the method of Campbell and Woodham [48]. The product was ground up with copper powder and sublimed at 350°/0.1mm. to remove any traces of halogen(yield 5.0 g.).
The mixture was extracted with xylene in a Soxhlet, the solution being replaced by fresh solvent at intervals of several hours. From the first fraction was obtained a large amount of 4,5:11,12-dibenzopyrene (LV) [49]. This was recrystallised from xylene and sublimed (Found: C, 95.6; H, 4.6. Calculated for $C_{34}H_{18}$; C, 95.8; H, 4.2%). It was identified by its

absorption spectrum and by a mixed melting point. (m.p. = 343-345°: mixed m.p. = 343-344°C.).

The next most soluble isomer was 1,2:11,12-dibenzoperopyrene (LII), which was similarly recrystallised, sublimed and analysed (Found: C, 95.8; H, 4.6%). It formed golden brown needles, m.p. 279°C.

1,2:6,7-Dibenzoperopyrene was the last isomer soluble in xylene.It was recrystallised and sublimed (Found: C, 95.8; H, 4.2%). This isomer (LIII) crystallised in orange prisms, m.p. 334-335°C.

Violanthrene (1,2:9,10-dibenzoperopyrene) (LVI) remained as an insoluble residue in the Soxhlet thimble. It was purified by repeated extraction with xylene and by sublimation. Its absorption spectrum and melting point (480°C) completed its identification.

These dibenzoperopyrenes all gave a blue colour in concentrated sulphuric acid.

No trace was seen of 7,7'-dibenzanthrylidene (LIV) or of isoviolanthrene (LVII).

(b) Condensation by a Zinc Dust Melt:- This was done in the usual manner [47]. Again 4,5:11,12-dibenzoperopyrene was formed in largest amount. Small amounts of (LII) and violanthrene (LVI) were present, and spectroscopic amounts of isoviolanthrene (LVII).

Condensation of 6,6'-, 8,8'-, and 6,8'-dimesobenzanthronyl.

8,8'-Dimesobenzanthronyl:- 8-Chlorobenzanthrone (4g.) was refluxed four hours in nitrobenzene (25 ml.) with copper powder (4.0g.). The solid product was filtered off and crystallisation from dimethylformamide gave yellow 8,8'-dimesobenzanthronyl, which was not further purified. More material was obtained on concentration of the nitrobenzene mother liquor.

3,4:11,12-Dibenzobisanthene (L).-

8,8'-Dibenzanthronyl (2.0 g.) was reduced for five minutes at 300° in a melt of zinc dust (6.0g.), sodium chloride (6.0g.) and zinc chloride (30g.). After washing the product, it was sublimed to give yellow 3,4:11,12-dibenzobisanthene (L), which was recrystallised twice from trichlorobenzene, to give 0.57g. of very small prisms. It was sublimed for analysis (Found: C, 95.6; H, 4.1. $C_{34}H_{16}$ requires C, 96.2; H, 3.8%). This compound melts at 432-433°, and dissolves very slowly in concentrated sulphuric acid to give a violet colour.

3,4:10,11-Dibenzobisanthene (LI).-

The eutectic mixture of 6- and 8-chloromesobenzanthrones

was refluxed (50g.) with copper powder (50g.) in nitrobenzene for four hours. The mixture was filtered hot and washed with nitrobenzene. Concentration of the filtrate gave 5.9g. of mixed 6,6'-, 8,8'- and 6,8'-dibenzanthronyls.

Mixed dibenzanthronyls (5.9g.) were reduced with zinc dust (15g.), sodium chloride (15g.) and zinc chloride (75g.) at 310° for 15 minutes. The product was purified by sublimation and crystallisation, but its spectrum showed it to be a mixture. Treatment with aluminium chloride gave no change in the spectrum. The mixture formed red prisms.(Found: C, 96.0; H, 4.0%). Chromatography on alumina gave poor separation.

Addition of Maleic Anhydride.- The mixture of dibenzobisanthenes (0.75g.) was melted with excess maleic anhydride and refluxed for two hours. Since the spectrum was little altered, chloranil (2.0g.) was added. After refluxing another 6 hours, the spectrum of (LI) had almost entirely disappeared. The reaction mixture was extracted with alkali and the adduct was reprecipitated. It was ground up with soda-lime and a little ethanol, decarboxylated at 300° and sublimed at 460°/0.02mm. A red-orange

hydrocarbon came off and was found from its spectrum to be mainly 3,4:11,12-dibenzobisanthene (L) together with a small quantity of circodiphenyl. Not enough material was available for separation to be attempted.

Attempted Syntheses of Circumanthracene [46].

"Controlled Graphitisation".

Reactions on Dinaphthoperopyrene (IL)-

(a) Dinaphthoperopyrene (IL) was ground up with soda-lime and slowly sublimed at 0.02mm under a stream of carbon dioxide which was bubbled through a mixture of chloroform and methylene chloride. Only starting material was obtained.

(b) Dichlorocarbene [61] was prepared in the presence of a benzene solution of (IL) at 0°C. Neither after stirring at room temperature nor after irradiation by a mercury lamp could any circumanthracene be detected.

(c) Diazoacetic ester was prepared in water and extracted with an ether solution of (IL). The solid which precipitated was dissolved in trichlorobenzene and examined in the spectroscope. It was mainly starting material though new absorption bands appeared at 576 and 513 mμ.

(d) Dinaphthoperopyrene was refluxed one hour with a 2:1 mixture of dichloroacetic acid and trichloroacetic acid. The colour soon changed from brown to red-violet. An acid product was filtered off and was decarboxylated

with soda-lime. Some circumanthracene may have been present but the yield was very poor. The acid was probably a 1,8-diacetic acid derivative of (IL).

(e) Dinaphthoperopyrene (0.1g.) was refluxed in benzene (20ml.) with aluminium chloride (0.5g.) and paraformaldehyde (0.1g.) for 110 minutes, during which another 0.5g. of aluminium chloride and several small portions of paraformaldehyde were added. The product contained some circumanthracene, which was oxidised during extraction of unreacted starting material with hot xylene. Repetition of this experiment gave no circumanthracene.

(f) Dinaphthoperopyrene (0.1g.) was refluxed for 30 minutes in a mixture of excess bromomaleic anhydride and chloranil, with a little nitrobenzene. The product (0.1g.) did not dissolve in alkali and was found to be the dibromo- compound.(Found: C, 72.3; H, 3.0. $C_{38}H_{16}Br_2$ requires C, 72.1; H, 2.5%).

Reactions on the Tetra-acid (LXI).-

(a) Tetra-acid (1.0g.) was treated with sodium formate (2.0g.) at 300° in a solution of potassium hydroxide (20g.) in methanol (20ml.). The yield was 4.0g.; 0.5g. of this was decarboxylated with soda-lime (2.5g.) and gave traces of circumanthracene.

The remaining material (3.3g.) was decarboxylated in quinoline (10ml) with copper powder (1.0g.). The product was mainly circumanthracene, which was oxidised during purification.

(b) Addition of various aldehydes to the tetra-acid in a melt of potassium hydroxide and methanol all gave similar spectra. Formaldehyde appeared to give the best results; it was added in small portions as paraformaldehyde. Decarboxylation of the product gave mainly (IL) with a spectroscopic amount of circumanthracene.

(c) Tetra-acid (5.0g.) was heated at 350° in an autoclave with paraformaldehyde (10g.), potassium hydroxide (30g.) and water (80ml.): the yield was 2.8g. No circumanthracene was produced on decarboxylation.

(d) Tetra-acid (1.0g.), zinc chloride (0.5g.) and potassium carbonate (4.0g.) were ground together and heated in a sealed tube at 295° for 17 hours. No acid or vattable material was produced. The product was mainly (IL), but showed a faint absorption band at 570 mμ.

7,7'-Dimethyl-1,9:5,10-diperinaphthyleneanthracene (LXIII).

This compound was synthesized as by Kelly [58],

except for the last stage, (LXVII) to (LXVIII). Standard conditions were found for this elimination: 50% KOH solution was dropped into a boiling solution of (LXVII) in quinoline; the water immediately came off, and wide distribution of the alkali was achieved. 0.43 ml. (0.215 g.) is the theoretical amount of KOH required for 1 g. of (LXVII); in practice, twice this amount was needed.

The later preparations(of the new isomer) required much larger amounts of alkali: (LXVII) (2.0g.) was treated with KOH (3.0g.) in boiling quinoline (20ml) for 20 minutes. Some of the product was dissolved in xylene and chromatographed on alumina. The first absorption band of (LXVIII) varied from 614 to 620 mμ during elution.

Recrystallisation of the crude product from benzene gave pure d,l-7,7'-dimethyl-1,9:5,10-diperinaphthylene-anthracene, m.p. 371°C. (Found: C, 94.8; H, 5.1. $C_{36}H_{22}$ requires C, 95.1; H, 4.9%).

The diol and chloro-compound melted at 346° and 365° respectively: Kelly [58] gives 329° and 359°, and 382° for (LXVIII).

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